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Howard, Hugh Wyman Jr.

Monterey, California. Naval Postgraduate School

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THE IDENTIFICATION OF NAVAL FUELS AND NATURAL FLUOROPHORS IN SEA WATER BY "FLUORESCENCE SPECTROMETRY"

Hugh Wyman Howard

NAVAL POSTGRADUATE SCHOOL
Monterey, California

THESIS

The Identification of Naval Fuels
and
Natural Fluorophors in Sea Water
by
"Fluorescence Spectrometry"

by

Hugh Wyman Howard, Jr.

Thesis Advisor: E. D. Traganza

March 1972

Approved for public release; distribution unlimited.

The Identification of Naval Fuels and Natural Fluorophors in Sea Water by "Fluorescence Spectrometry"

by

Hugh Wyman Howard, Jr.
Lieutenant, United States Navy
B.S., United States Naval Academy, 1965

Submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE IN OCEANOGRAPHY

from the

NAVAL POSTGRADUATE SCHOOL
March 1972

ABSTRACT

Fluorescence and Excitation spectra of Navy Standard Fuel Oil (NSFO), Navy Distillate Fuel (ND), Diesel Fuel and Navy Aircraft fuels (JP-4 and JP-5) were obtained with the Turner 210 Absolute Spectrofluorometer. Excitation spectra (peaks at 320 nm, 240 nm, 250 nm, 270 nm, 250 nm respectively) and Fluorescence spectra (peaks at 350, 410 nm, 330 nm, 340 nm, 240, 325 nm, 240 nm respectively) are characteristic and may allow selective identification of these fuels. Quantitative determinations by fluorescence analysis of ND fuel oil extracted from sea water samples, with cyclohexane, showed saturation values of approximately 11 ppm. An all glass, in-situ vacuum filtering water sampler was designed and built for collection of filtered (.45μ glass) noncontaminated sea water samples for the fluorescence analysis determination of the natural background fluorescence of the Monterey Bay region. Fluorescence spectra of sea water from Monterey Bay, obtained on board R/V ACANIA, and samples from the Arctic Ocean, showed broad banded emission in the region of 450 nm.

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I. INTRODUCTION

Fluorescence in sea water is not new [Kalle 1937, Shtegman 1966, Traganza 1967, Monizikoff 1969]; however, the practical application of its measurement in sea water is only beginning to be appreciated or utilized.

The increasing frequency of oil spills both reported and not, is reaching alarming proportions. Fluorescence offers both active and passive identification of oil pollution and may be an answer to problems of monitoring, detecting and evaluating the source of common contaminating fuel oils.

Oil discharged into the ocean will form slicks which eventually spread and cover large areas. The danger to marine life is mostly due to oil dissolved in the bulk of the sea water [Parker 1967].

One of the first attempts to investigate the natural fluorescence of marine waters was Kalle's study of Gelbstoff as early as 1937 [see Kalle 1966]. Interest in the study of fluorescence in sea water continued with Shuleikins (1953) investigation of sea water coloration [Shtegman 1966]. Traganza (1967) studied fluorescence and excitation spectra of dissolved organic matter in sea water.

Traganza's spectral analysis of sea water shows a contrasting picture of broad band background spectra against transient characteristic spectra of natural biological origins. The suggestion is that the natural fluorescence

of the ocean provides a broad banded low level background against which the fluorescence from recent biological or other events such as trace oil contamination from a distant spill can be detected.

The determination of organics, which are responsible for the natural background fluorescence, will involve the difficult task of isolating and concentrating minute quantities of organic matter in sea water. Monizikoff (1969) used fluorescence and certain concentrating and extraction processes to selectively identify several fluorescent substances present in sea water.

In the past, a major limiting factor to the study of dissolved organics in the ocean, was the lack of suitable instrumentation, capable of detecting the trace quantities of organics in "salt water." "On the average, every gram of organic matter is dwarfed by 36,000 grams of salts in 900,000 grams of water" [Diehl 1971].

Recent development of sophisticated and sensitive fluorescence spectrophotometers with better resolution may substantially improve the capability for analyzing trace amounts of organics. In some cases, direct analysis may be possible, but in any case, where a fluorescence technique is applicable, one will not be faced with the problem of processing inordinately large volume of sea water samples. This in itself should improve the probability of getting real time synoptic data on organics in the ocean.

An excellent discussion of various instruments may be found in Udenfriend (1962). Turner (1964) adds to this with a good description of one of the most sophisticated instruments available today. Aminco Bowman Corporation is advertising an instrument with a sensitivity of parts per trillion.

This paper is directed toward the development of routine methods for fuel oil contamination analysis, yielding type, source and concentration of the pollutant.

The results of this work may provide a foundation from which the Navy can develop a system capable of reliable, simple, economical and continuous, monitoring and prevention of potentially critical pollution levels in sea water. Detection and positive identification of the fuel oil pollution sources is the final objective.

II. BACKGROUND

A. HISTORY OF FLUORESCENCE ANALYSIS OF FUEL OIL

The cumulative literature indicates that "passive fluorescent tracing" is a promising though little utilized method for the detection of many organic compounds in the ocean including petroleum products. "Active methods" in which water or oil is spiked with a known fluorescent material also offers a variety of possible applications. [See Rieker 1962], Bentz and Strobel (1933) examined fluorescence of oil resulting from excitation with a mercury vapor lamp. It was noted that refined oils fluoresced in the blue region while crude oil fluoresced in the brown and yellow region. Melhase (1936) found that no two samples of California crude oils fluoresced with the same shape spectra or intensity unless they were from the same parent oil sand. Work done by Shuldiner (1951) reported that oil spills in harbors could be matched with standards by comparing the shape and color of paper chromatograms under ultra violet excitation. His method was successful in collecting identification information sufficient for prosecution and conviction of oil polluters on the East Coast of the United States of America. [See Parker 1962]. Kats and Sederov (1954) have analyzed fluorescence spectra of various crude oils and their fractions. They proposed that fluorescence spectra be utilized as a method for identifying crude oil and various petroleum

products. Mihul, Ruscior and Pop (1956) studied the fluorescence spectra of various oils and suggested that fluorescence be used to identify petroleum products from various sources.

C. A. Parker, et al. (1967) utilized fluorescence analysis to determine the concentration of oil in sea water and plankton, resulting from the Torrey Canyon oil spill. Thruston and Knight (1971) were able to comparatively identify several fuel oils by two methods of characterizing each fuel oil; first the ratio of shoulder to peak intensity for each undiluted fuel and second, the shoulder to peak ratio for various dilutions of the same fuel (Fig.37). A. W. Hornig (1971) illustrated a number of materials in the ocean which may be detected and identified by fluorescence. One of these is a number-two fuel oil. He suggests that other crude oil samples will have signature variations which may allow identification of the oil. The fact that various petroleum products can be made to fluoresce characteristically is significant and common to all of these efforts.

III. METHODS

A. SEA WATER SAMPLING AND HANDLING PROCEDURES

Marine water samples were taken on 2 November 1971, aboard R/V ACANIA at stations established by Lewis (1970). The stations are described in Table 1 and Fig. 1. Station selection was based upon the probability that, where water samples would most exhibit fluorescence. The samples were taken at three depths in order to establish a general spatial pattern for the distribution of organic matter. Samples were also collected in the Arctic at Point Barrow Research Station in 50 feet of water.

Surface samples were obtained by lowering a 125 ml brown bottle sampler (Figs. 2 and 3) which was opened from the surface by a lanyard attached to the ground glass stopper.

Midwater samples were collected utilizing a specially designed, all glass, in-situ vacuum filtering device (Fig. 4 through 8). The sampler is supported in a stainless steel housing on which the trip release is attached. The glass portion of the sampler consists of the components shown in Fig. 7.

A precombusted 0.45μ filter was placed in the sampler and the rig was lowered to the desired depth. At this point a weight was released on the hydro wire to actuate the

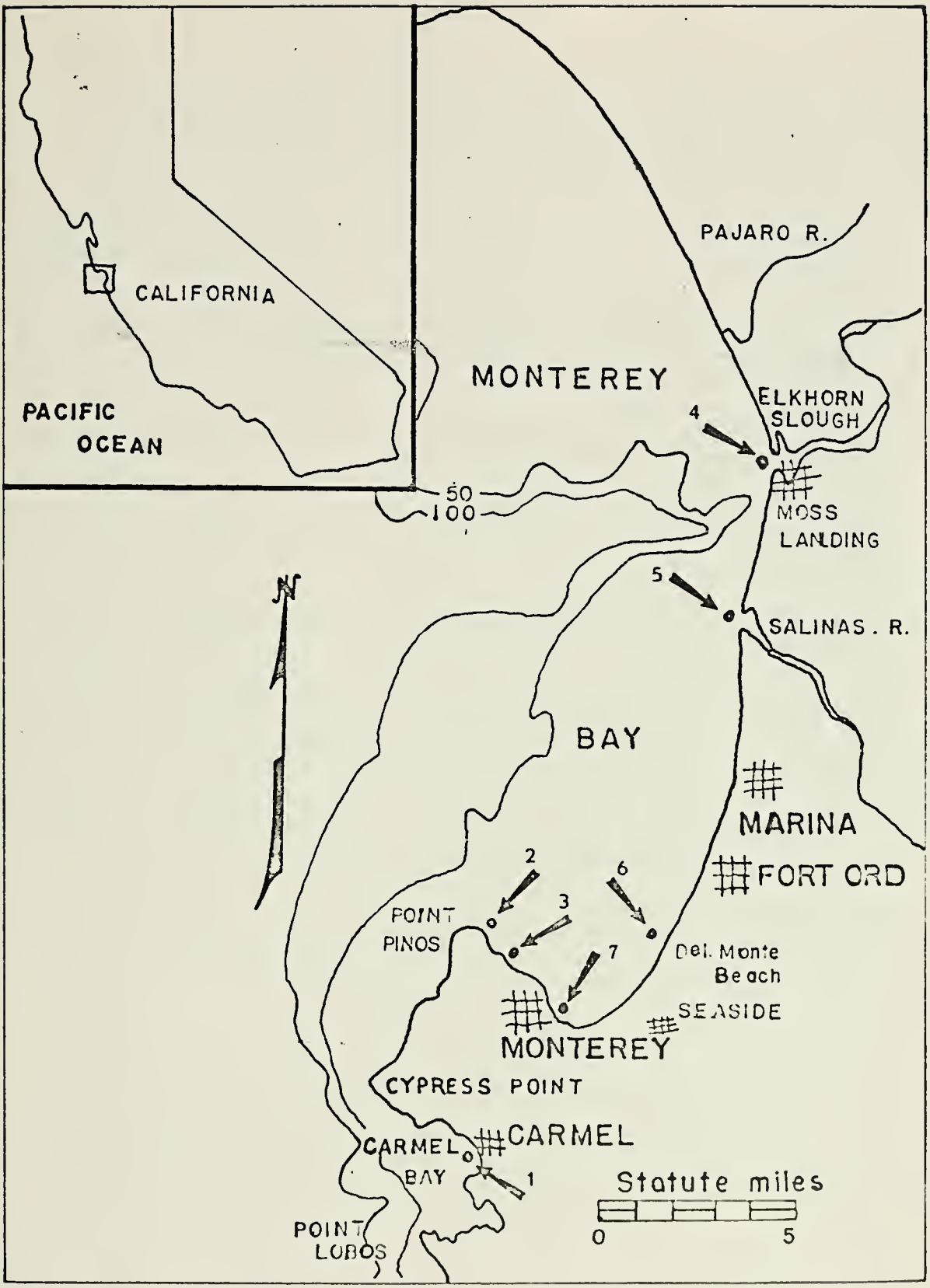

Fig. 1. Chart of sampling stations utilized for collection of sea water samples for Fluorescence Analysis.

TABLE 1. WATER SAMPLE STATIONS IN MONTEREY BAY

Station Number	Position	Type	Sample Depth
1	126° 56.0'W 36° 33.0'N	Sewage outfall Carmel Bay, Calif.	Surface 50 ft 100 ft
2	121° 55.9'W 36° 38.3'N	Sewage outfall Pacific Grove, Calif.	Surface 30 ft 60 ft
3	121° 54.8'W 36° 37.6'N	Kelp beds	Surface 50 ft 100 ft
4	121° 47.5'W 36° 48.3'N	Industrial discharge	Surface 30 ft 60 ft
5	121° 46.7'W 36° 44.8'N	Salinas River	Surface 30 ft 60 ft
6	121° 50.6'W 36° 37.7'N	Rip current Del Monte Beach, CA	Surface 50 ft 100 ft
7	121° 53.3'W 36° 36.3'W	Monterey Harbor	Surface 20 ft

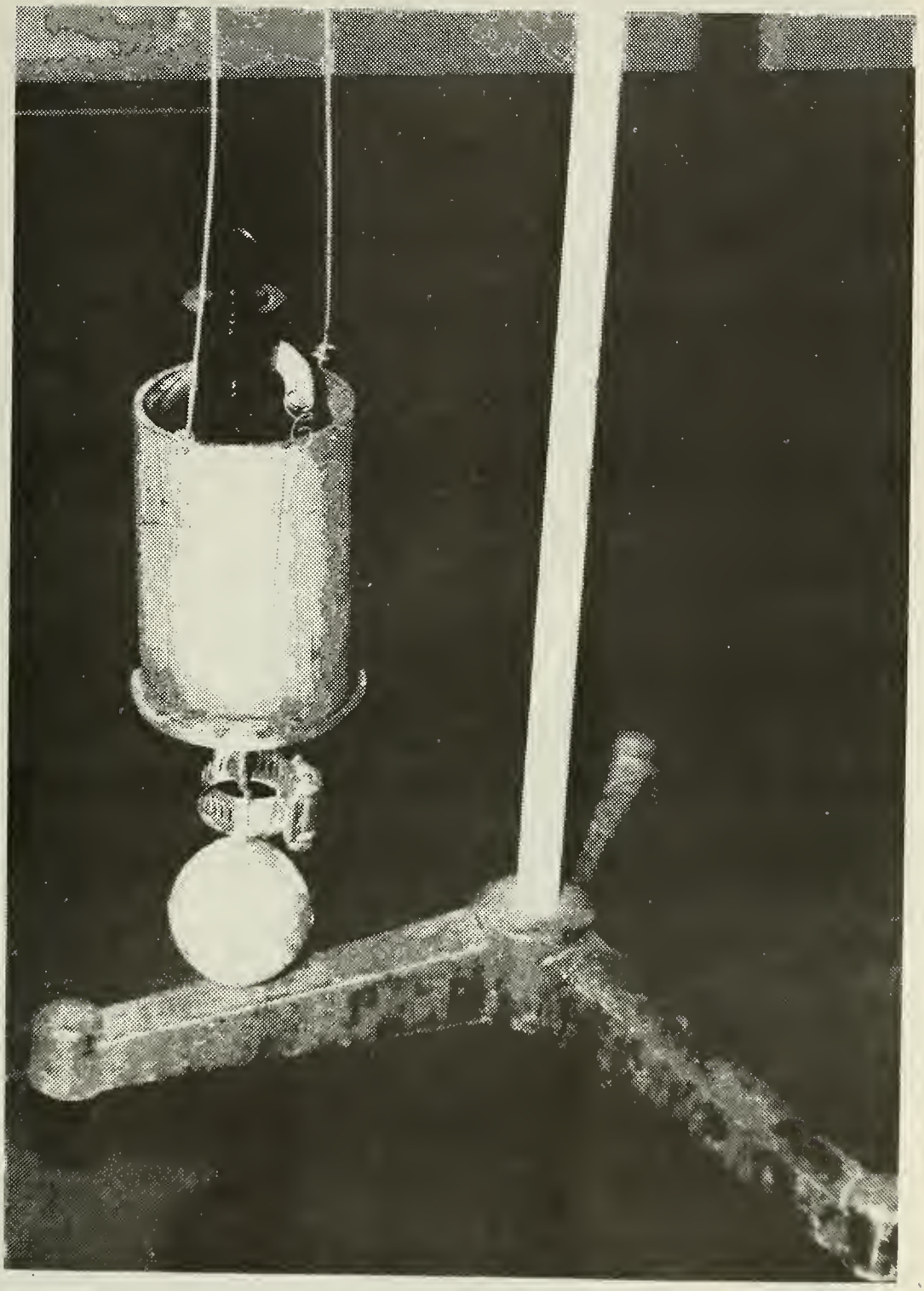

Fig. 2. Surface 125 ml ground glass stoppered sampling device for collection of sea water samples for Fluorescence Analysis.

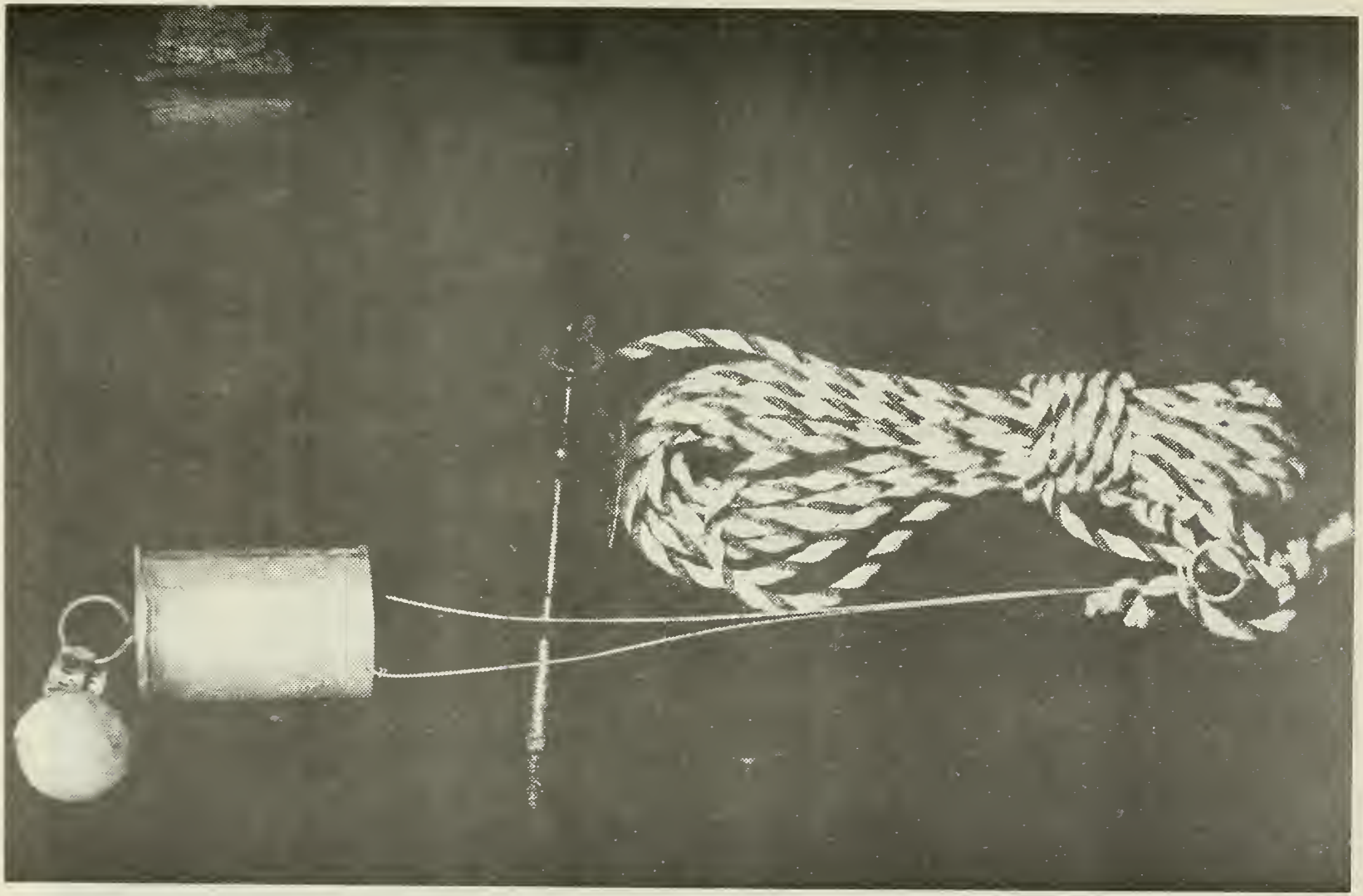

Fig. 3. Components of a surface sea water sampling device for Fluorescence Analysis.

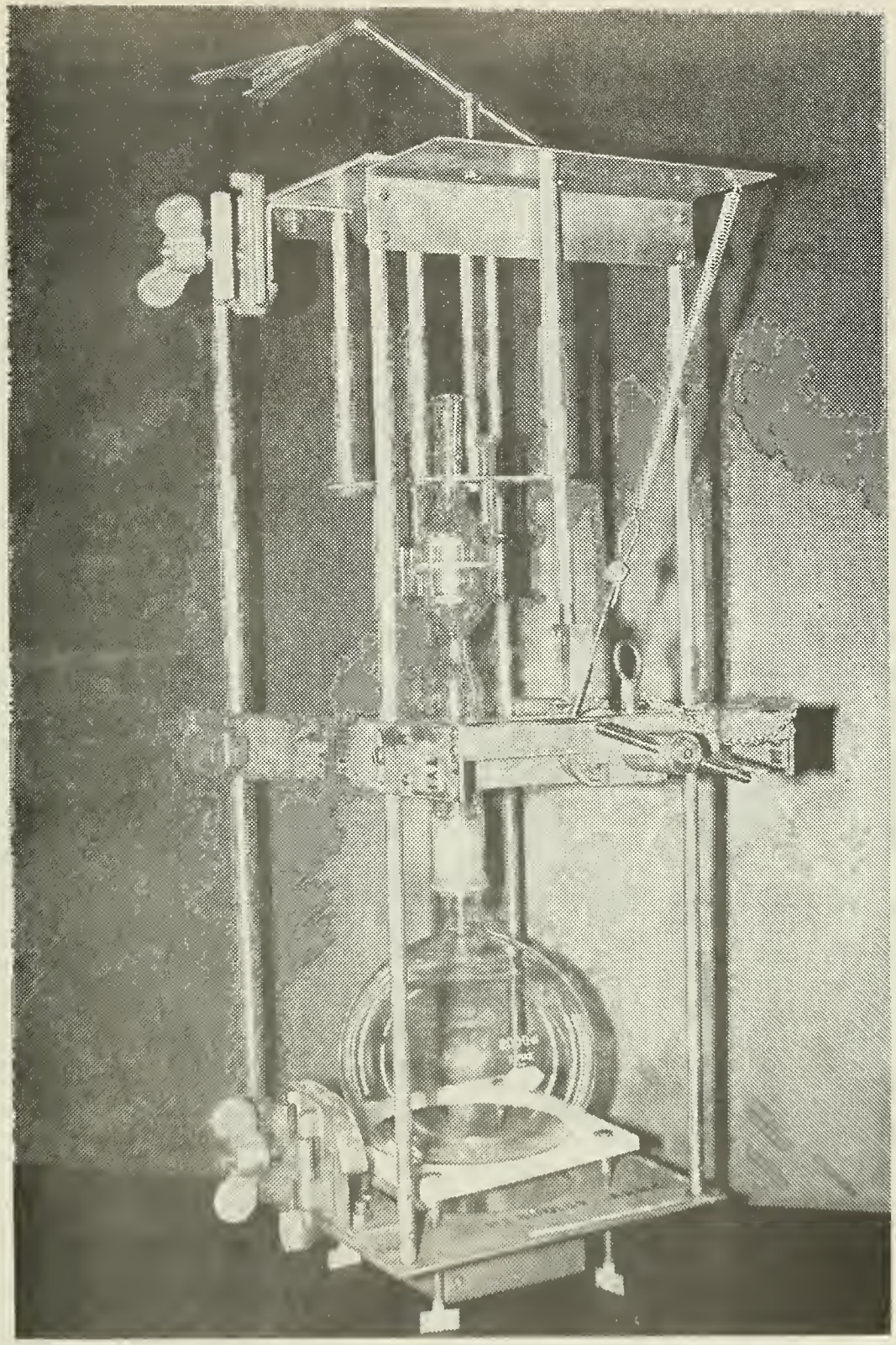

Fig. 4. An all glass, in-situ vacuum filtering (0.45μ glass filter) water sampler for fluorescence analysis of sea water.

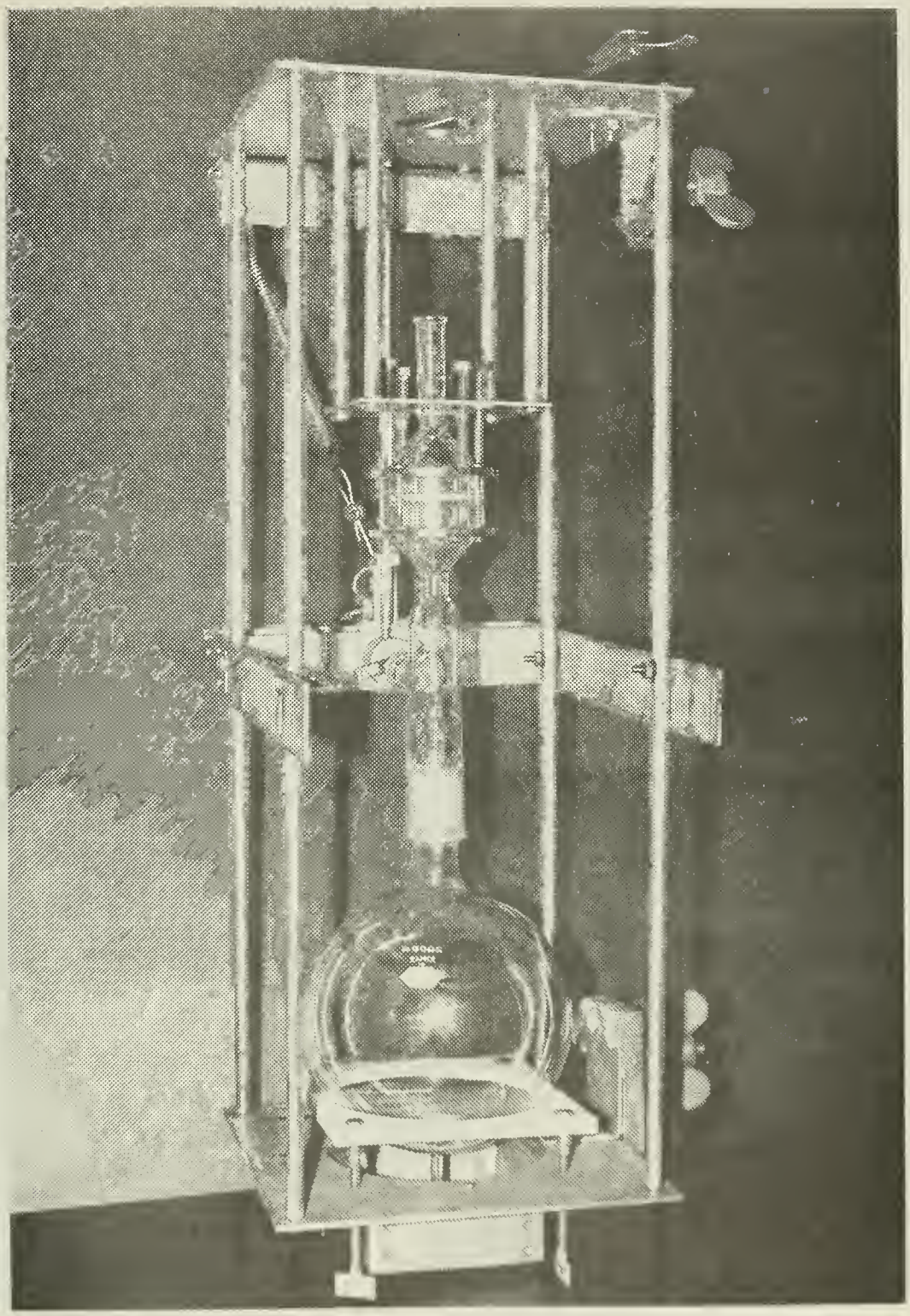

Fig. 5. An all glass, in-situ vacuum filtering sea water sampler.

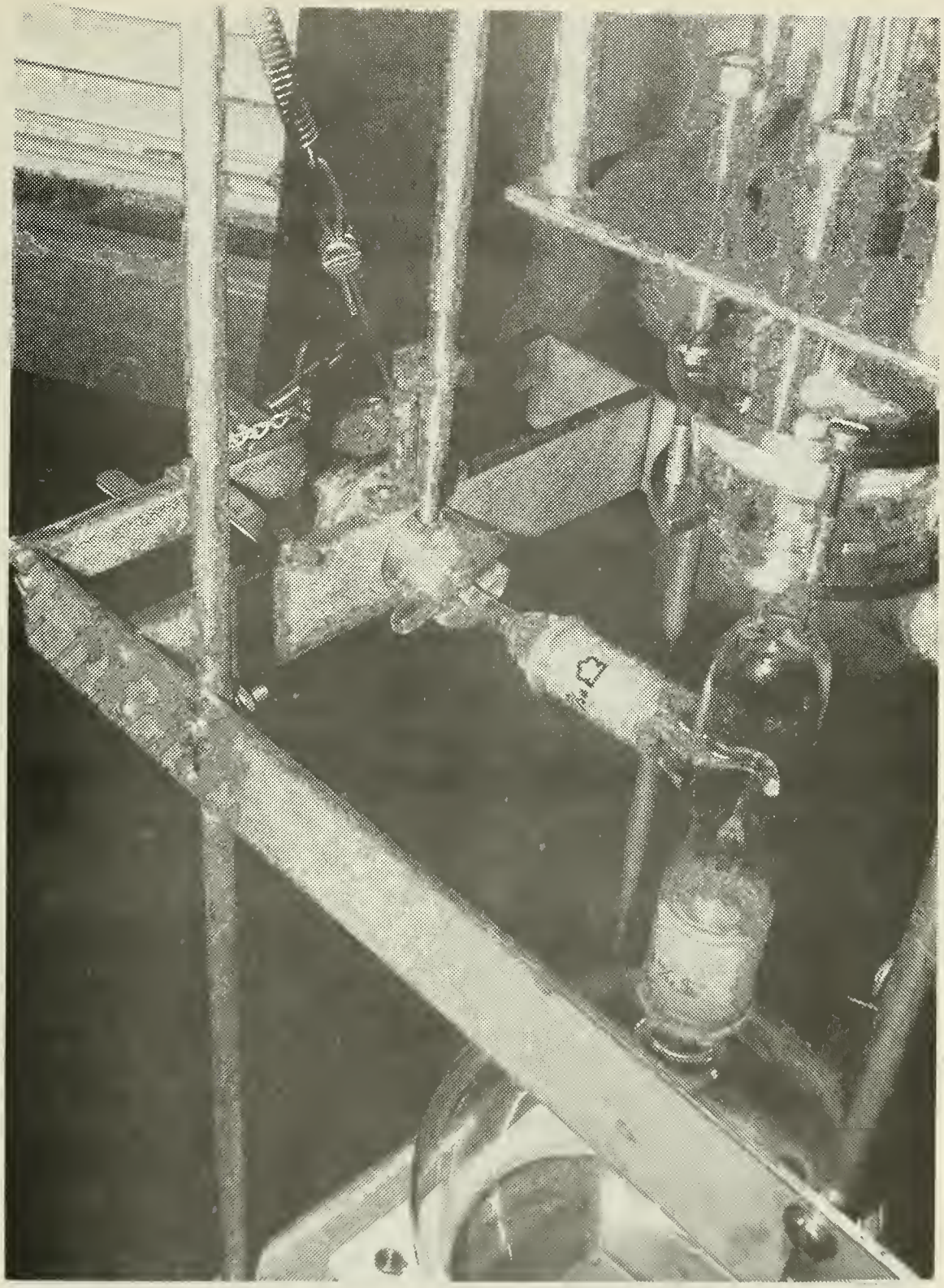

Fig. 6. Valve and actuator system for an all glass, in-situ vacuum filtering sea water sampler.

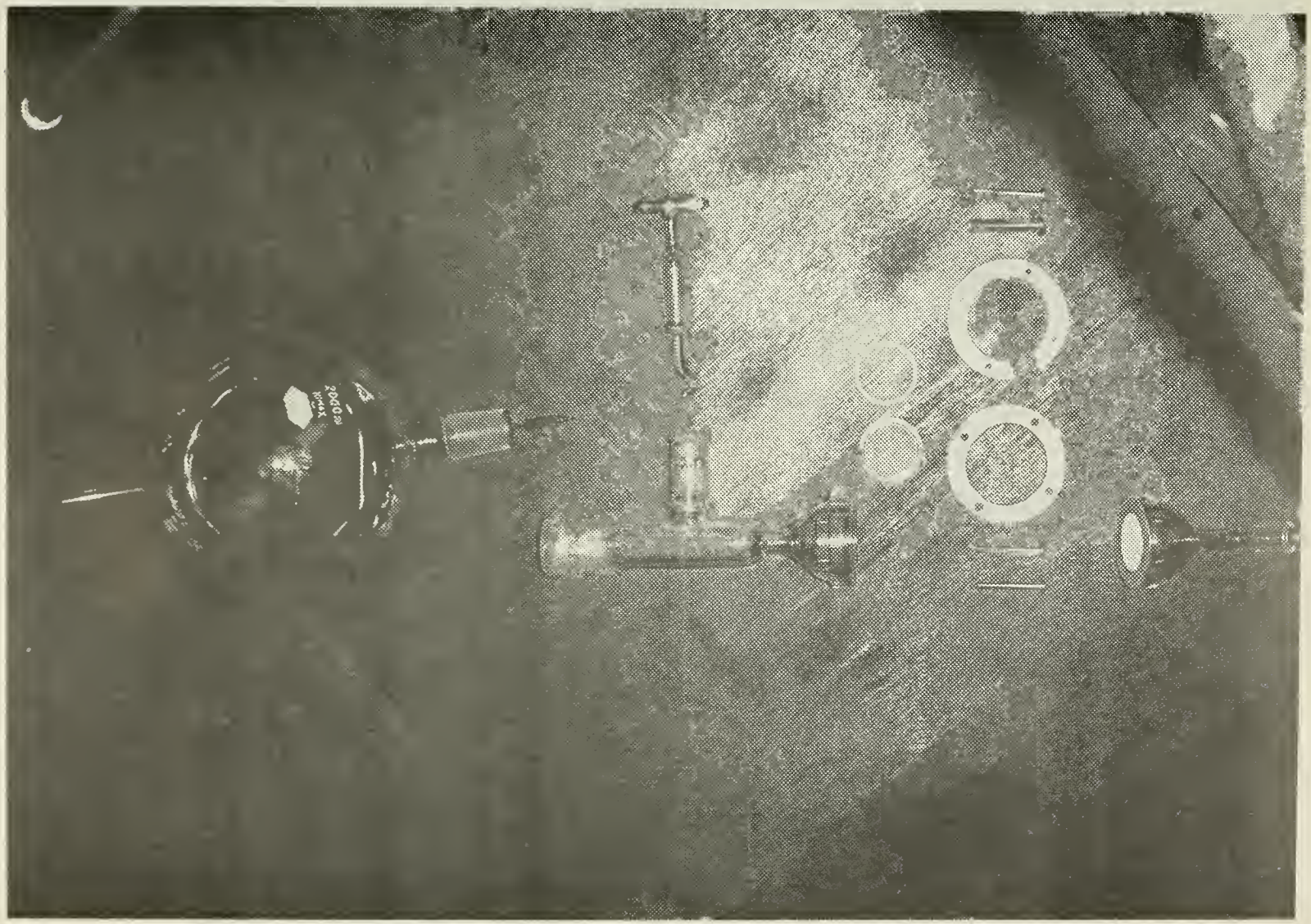

Fig. 7. Components of all glass, in-situ vacuum filtering sea water sampler.

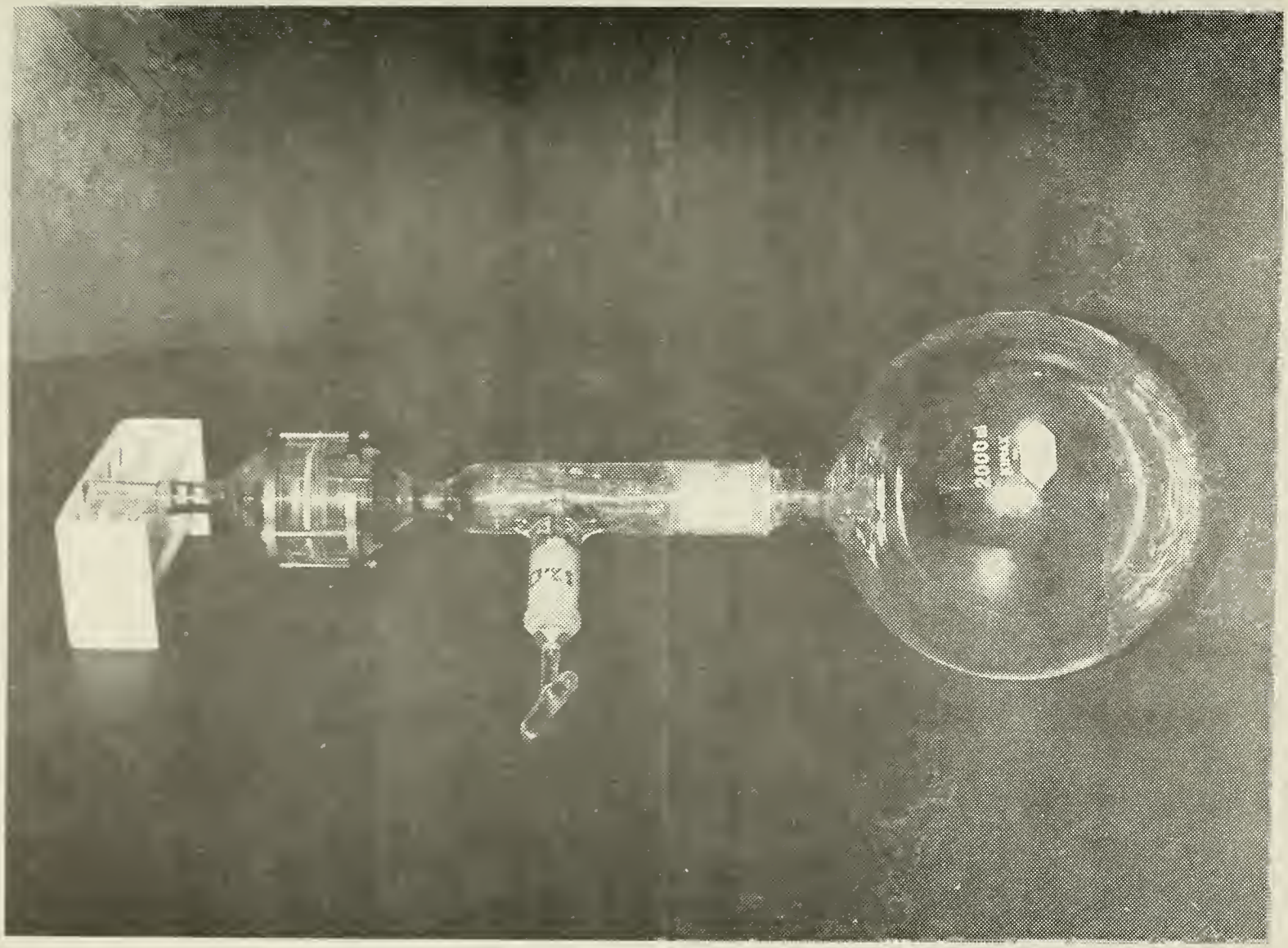

Fig. 8. Assembled sampling flask and filtration system for all glass, in-situ vacuum filtering sea water sampler.

spring tension, rotating valve system, which breaks a glass tip. This allowed the vacuum to withdraw a sample into the two liter sample collection flask. A battery of pre-evacuated flasks was taken on the cruise to collect individual samples. Nonfiltered mid-water samples were collected utilizing evacuated glass tubes of two liter capacity. They were lowered to the desired depth on an aluminum support frame and actuated by releasing a weight attached to the hydro wire to break the tips extending from the evacuated glass tube samplers.

Bottom water samples were collected by pouring off the water recovered along with bottom sediments in a "Shipek" sampler.

The surface and bottom samplers were separated into filtered and unfiltered samples.

B. FILTRATION PROCEDURES

Samples were contained in specially cleaned brown glass, 125 ml, sample bottles. The filtration unit was constructed of a 300 ml Millipore funnel, with a Teflon seal, mounted on a fritted glass base attached to a vacuum cell (Fig. 9). The sample bottle was placed inside this cell to receive the filtered sample. This one step filtration minimizes possible contamination. The samples were stored at 10°C in the specially cleaned and combusted, 125 ml sample bottles.

Prior to each filtration run, a glass filter (0.45μ) was inserted after being combusted at 400°C to oxidize organic

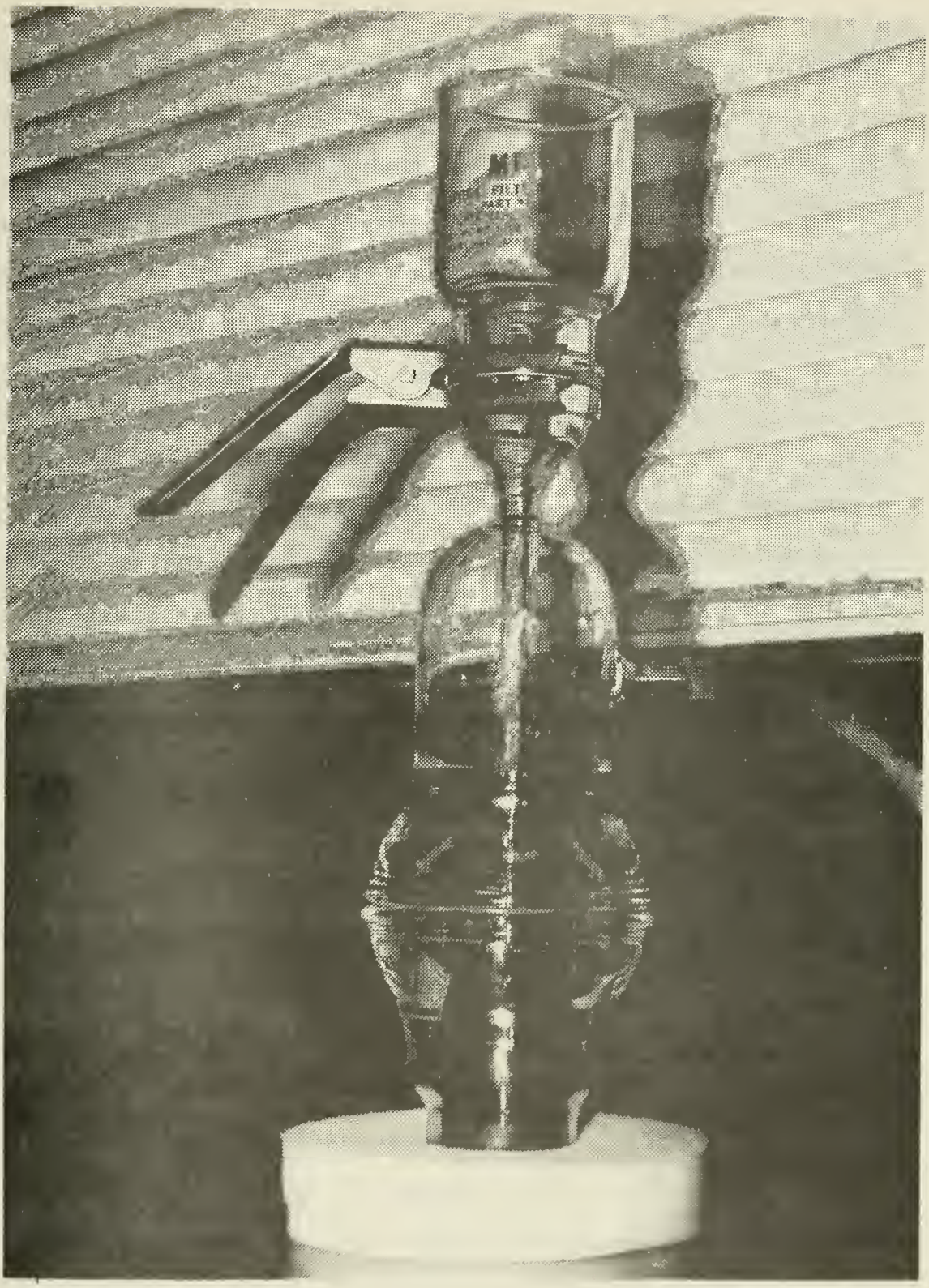

Fig. 9. "Bell Jar" filtration unit with 125 ml, brown glass, sampling bottle positioned inside the vacuum dome.

matter in the filter. The filter support was thoroughly cleaned by repeated flushing with distilled water.

An improvement was made to this filtration system by replacing the fritted glass filter support with a ground glass base and stainless support screen with Teflon gasket. This unit seals better and is easier to clean and allowed further minimizing of contamination problems (Fig. 7).

C. CONTAMINATION PREVENTION

Five general rules were adopted to prevent contamination. No polyethylene, rubber, cork or organic compound was used as a bottle, stopper, sampler or allowed to come in contact with the sampler [Lewis 1971]. All glassware was thoroughly scrubbed with biodegradable soap, preferably Calgon due to its low residual fluorescence blank after rinsing [Traganza 1969], and followed by a distilled water rinse. The glass was then cleaned in chromic acid and sulfuric acid followed by rinsing with acetone. This was followed by several rinses in organic free distilled water. This water was treated with 5 grams per liter of potassium persulfate and allowed to stand overnight. All exposed sample storage vessels were covered with aluminum foil after cleaning. Promptly after sample collection and filtration, the sea water was refrigerated to cut down on degradation. Filter contamination was minimized by precombustion at 450^{o}C for 4 to 6 hours. Filters were stored in aluminum foil [Diehl 1971]. Instrument cuvettes were

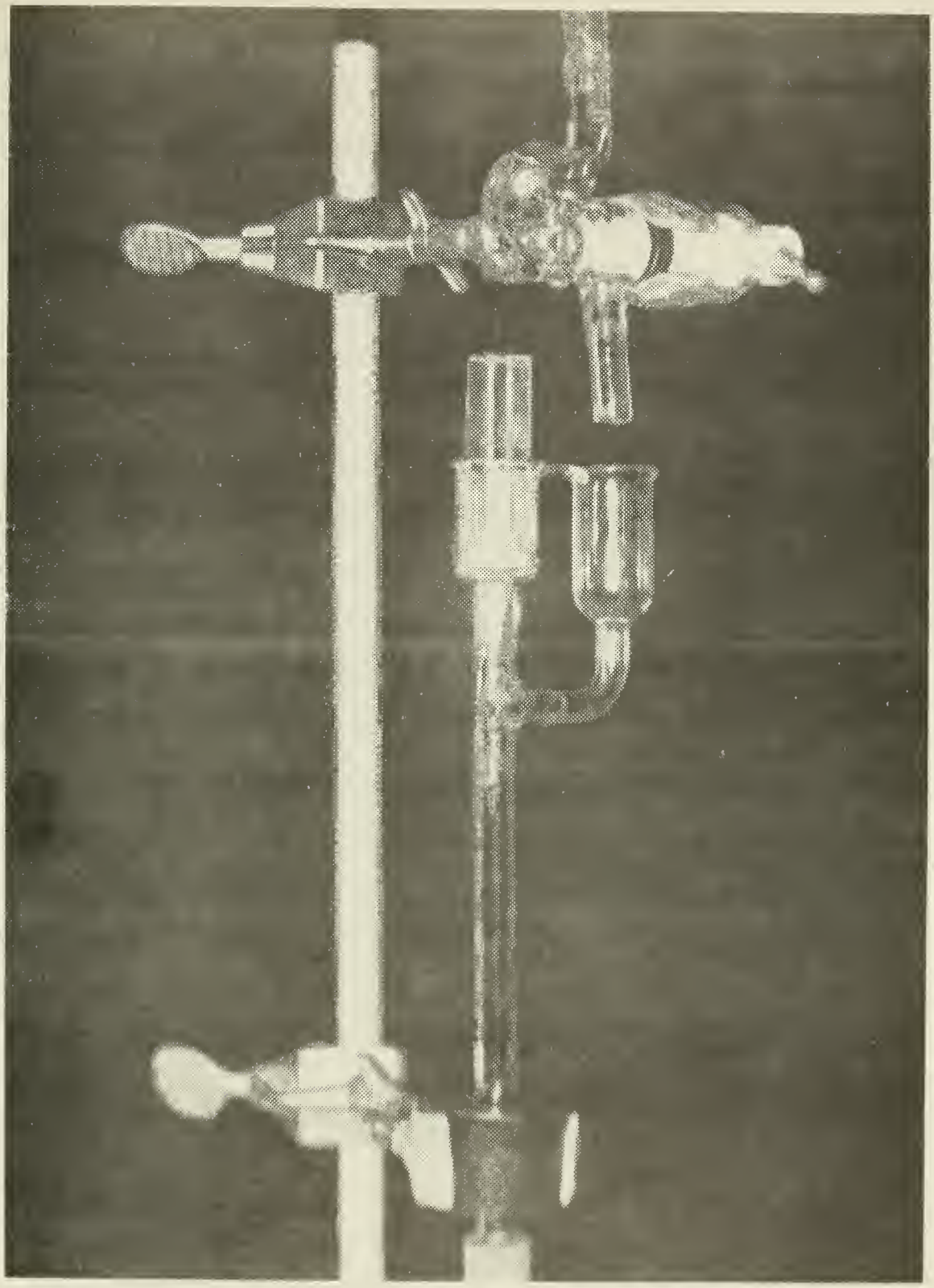

Fig. 10. 4 ml, fluorescence analysis, cuvette washing apparatus.

washed with soap and rinsed with water followed by acetone and organic free distilled water. The glass cuvette cleaning apparatus (Fig. 10) was used.

D. FLUORESCENCE ANALYSIS OF MONTEREY BAY AND ARCTIC OCEAN SEA WATER SAMPLES

Each 125 ml sea water sample was analyzed in turn on the Turner 210 Absolute Spectrofluorometer (Fig. 11 & 12) utilizing the uncorrected fluorescence mode of operation. The samples were excited at selected wavelengths from 200 nm to 500 nm. Particular care was taken to ensure that the sample cuvette was specially cleaned prior to each run. After exploratory excitation and emission spectra were completed, the instrumental settings were selected to provide the best possible characteristic trace.

E. SELECTIVITY EXPERIMENT FOR FLUORESCENT TRACING OF COMMON NAVAL FUELS

Five Naval fuels were investigated; Navy Distillate (ND), Navy Standard Fuel Oil (NSFO), Diesel Fuel (DF), and two Aircract fuels (JP-4 and JP-5).

Each fuel was diluted successively in Spectro quality cyclohexane to 10^{6}, 10^{5}, $5x10^{4}$, $2x10^{4}$, 10^{4}, 10^{3}, 10^{2}, 10^{1}, 10^{-1} and 10^{-2} ng/ml (i.e. 1000, 100, 50, 20, 10, 1.0, 0.1, 0.01 ppm and 0.1, 0.01 ppb).

The samples were placed in specially cleaned glassware to avoid contamination (see above). Each fuel type was excited from 200 nm to 500 nm in 50 nm steps. After pre-

liminary searching, characteristic traces of each fuel were obtained (see Fig. 19 through 26).

F. QUANTITATIVE DETERMINATION OF OIL CONTENT IN A KNOWN PERCENT SATURATED, NAVY DISTILLATE IN SEA WATER, SAMPLE

A saturated solution of Navy Distillate in sea water was diluted with sea water from 100% to 10% saturation in steps of ten. The saturated solution was obtained by vigorous shaking of Navy Distillate and sea water and allowing to stand for several weeks.

Each sample was excited at 310 nm to determine its initial fluorescence spectrum. Six milliliters of "Spectro-quality" cyclohexane was added to each sample in a separatory funnel. After shaking vigorously 3 times, the samples were left standing for 4 hours. The sea water was then drawn off and examined on the fluorometer in the uncorrected mode. The extract was also examined. Curves were obtained of fluorescence intensity of sea water before and after extracting against percent saturation.

The samples and extract were then returned to the separatory funnels and an additional milliliter of cyclohexane was added and shaken. After standing overnight, the fluorescence intensity was again recorded.

It was suspected after observing the results for the above that pre-centrifugation of the sea water would eliminate any inconsistencies in fluorescence intensity associated with oil globules in the water samples.

Ten milliliters of 10, 30, 50, 70, 90 and 100% saturated ND in sea water was placed on the centrifuge for 5 minutes at medium speed. Five milliliters was withdrawn at the bottom of the aliquotes with a pipette and examined on the fluorometer. Excitation was at 310 nm. The samples were placed in separatory funnels and 10 ml cyclohexane was added. After standing for a period of 4 hours, the fluorescence spectra were recorded separately for sea water samples and extract.

The data collected was plotted on semi log paper to determine the relationship between the concentration of oil and the fluorescence intensity.

Known amounts of Navy Distillate were dissolved in cyclohexane to establish standard curves of fluorescence versus concentration (Fig. 32). The samples were excited at 290 nm. The extract from above was compared to these curves to determine the amount of oil in the extract and by extrapolation to determine the concentration of oil in each oil-sea water sample.

G. RELIABILITY

1. Sensitivity

In order to determine the lowest concentration of fuel oil detectable with the Turner instrument, the following procedure was conducted.

A serial dilution was made of Navy distillate fuel in "Spectroquality" cyclohexane and in sea-water. Each

serial dilution was excited at the characteristic wavelength for Navy Distillate (290 nm) and the fluorescence spectrum was recorded.

The object was to determine the lowest concentration detectable with the instrument at the proper settings for maximum sensitivity.

2. Precision

Instrumental precision was established by replicate excitation of a known standard over a 4 hour, 45 minute period. The standard was quinine bisulfate in 10^4ng/ml (10 ppm) solution, with H_2SO_4.

The fluorescence spectra were recorded for the characteristic peak excitation wavelengths of 250 nm and 350 nm. The fluorescence maximum was observed at 460 nm.

Precision was also established for the extraction experiment by fluorescence analysis of 3 replicate samples of Navy Distillate fuel at 50% and 5% saturation in sea water, before and after extraction.

Comparison of the fluorescence maximum intensities yielded a standard deviation for the process.

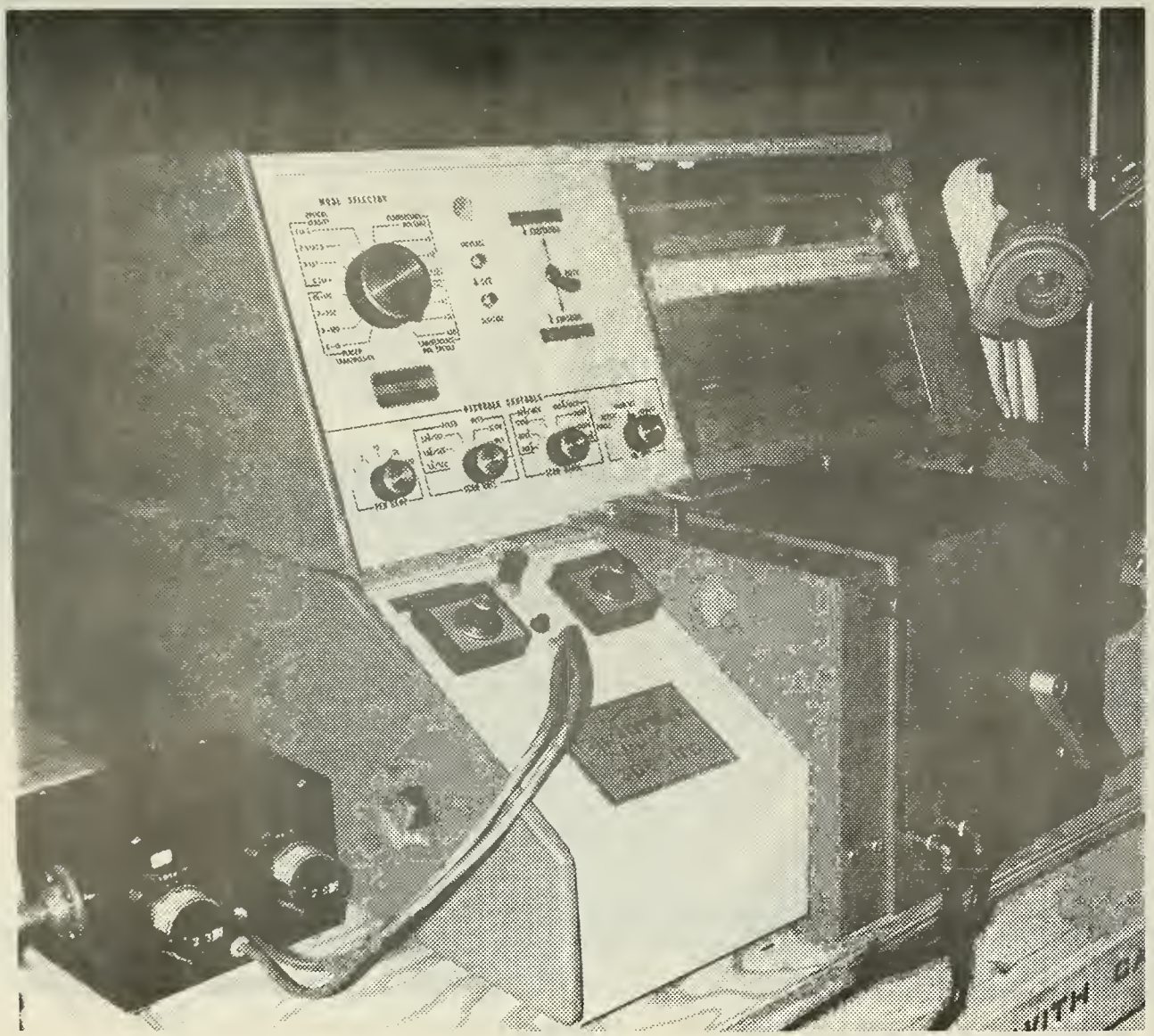

Fig. 11. Turner 210 Absolute Spectrofluorometer.

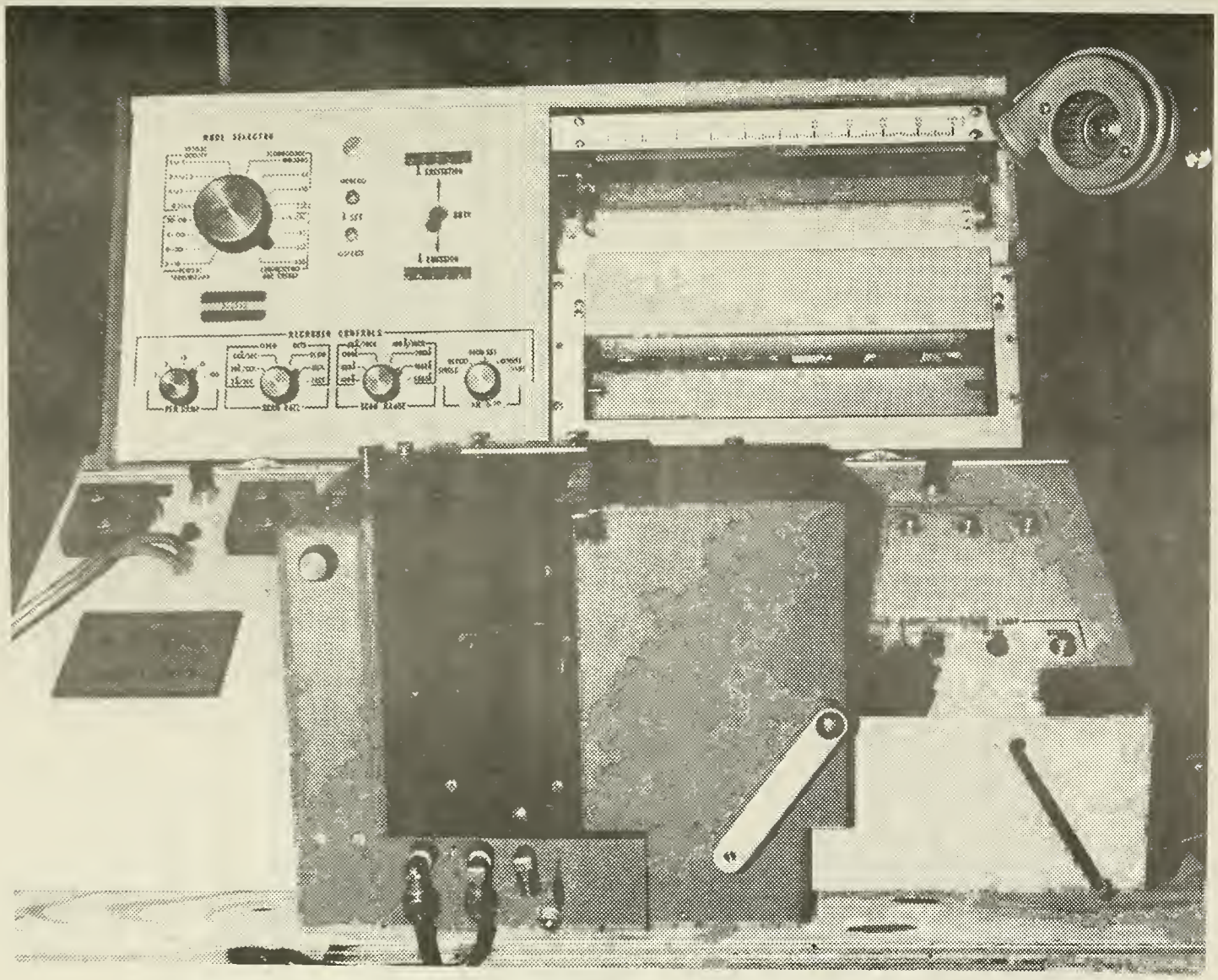

Fig. 12. Front control panel, recorder group and open sample compartment of Turner 210 Absolute Spectrofluorometer.

IV. RESULTS

A. BACKGROUND FLUORESCENCE OF MONTEREY BAY AND THE ARCTIC OCEAN

Sea water samples fluoresced in response to ultraviolet excitation. Common mineral salts and end products from the decomposition of organic matter were assumed to have no influence on this mission [Hornig 1971, Shtegman 1966].

Fluorescence spectra of marine waters were broad essentially featureless bands in the region of 450 nm (Fig. 14 through 17). The maximum excitations for this fluorescence ranged from 310 nm to 350 nm.

An attempt was made to separate the fluorescent organic structures present in the sampled regions, by utilizing high instrumental sensitivity and excitation energy with various optimum slit widths, to provide good resolution. The results were disappointing and agreed with work done by Sinel-'nikov and Ryzhekov [Shtegman 1966] who concluded that fluorescence spectra did not selectively identify the composition of natural waters; however, they are capable of detecting recent events in the water column. Traganza (1969) showed recent biological events are detectable and that individual background fluorescent compounds may be selectively identified when fluorescence techniques are properly combined with suitable concentration and isolation procedures.

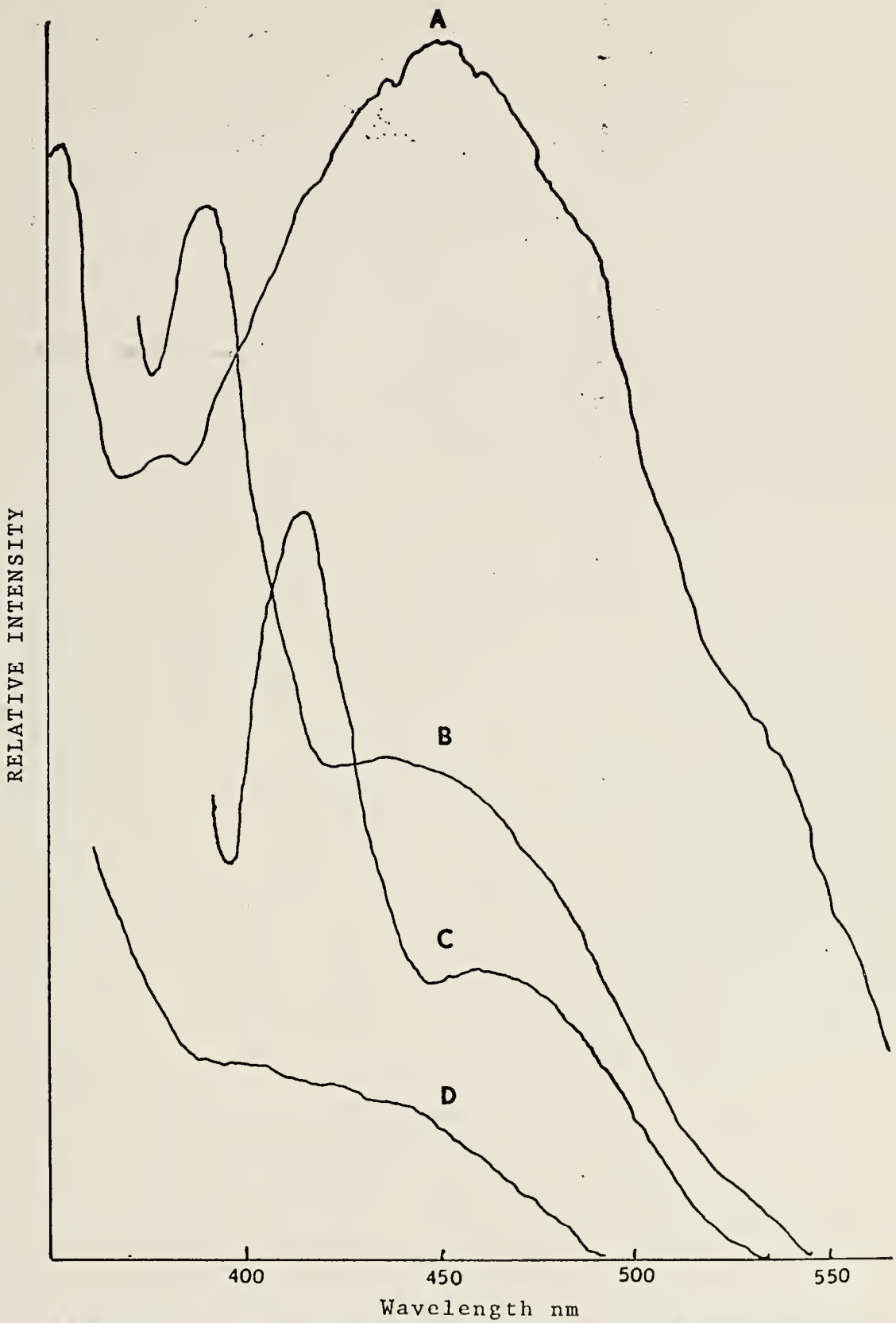

Fig. 13. Fluorescence spectra of surface sample of nonfiltered sea water from station one (Fig. 1). Excitations are: A, 220 nm; B, 340 nm; C, 360 nm; D, 200 nm.

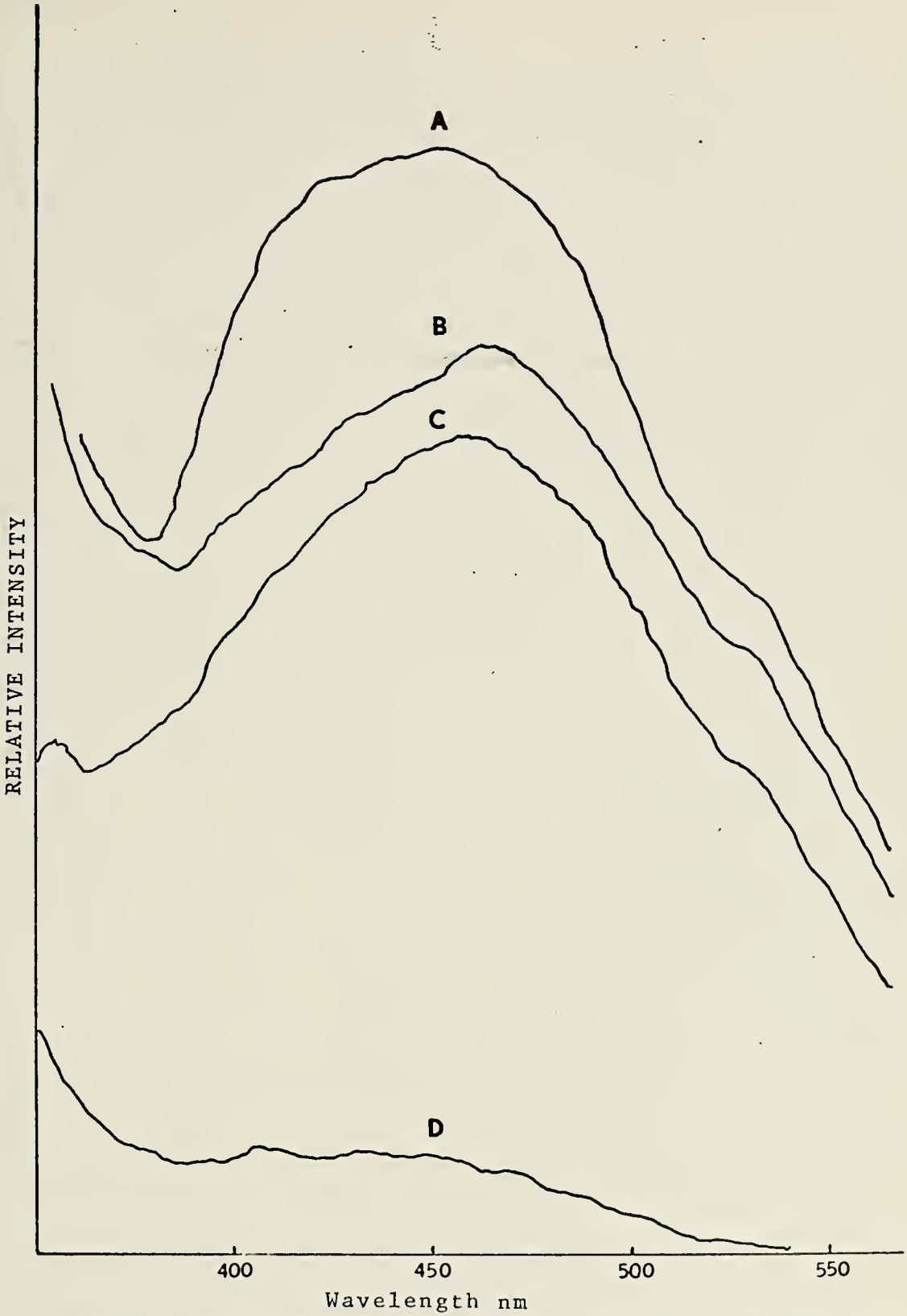

Fig. 14. Fluorescence spectra of a nonfiltered bottom sample of sea water from station one (Fig. 1). Excitations are: A, 310 nm; B, 290 nm; C, 250 nm; D, 220 nm.

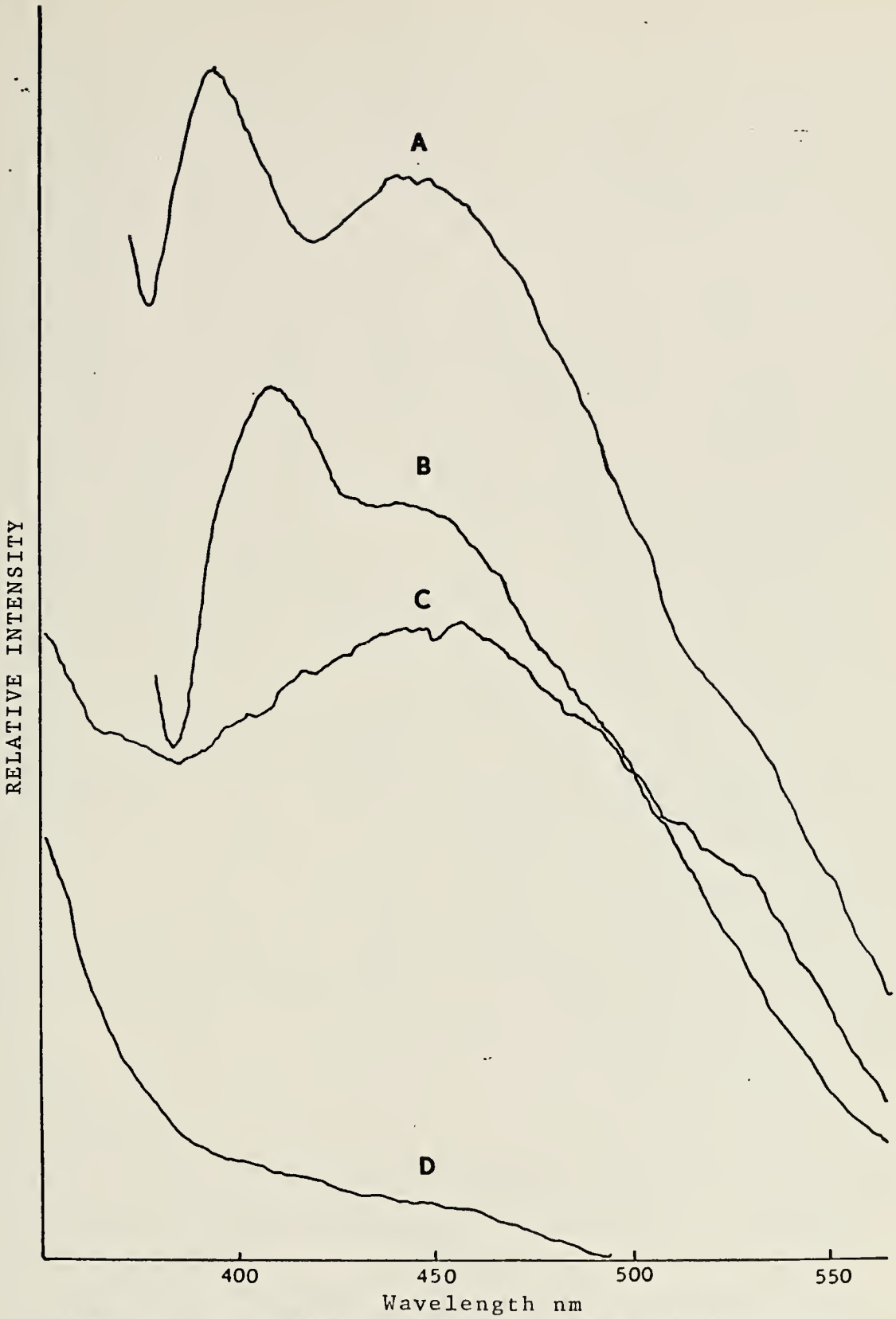

Fig. 15. Fluorescence spectra of a filtered bottom sample of sea water from station one (Fig. 1). Excitations are: A, 340 nm; B, 370 nm; C, 250 nm; D, 220 nm.

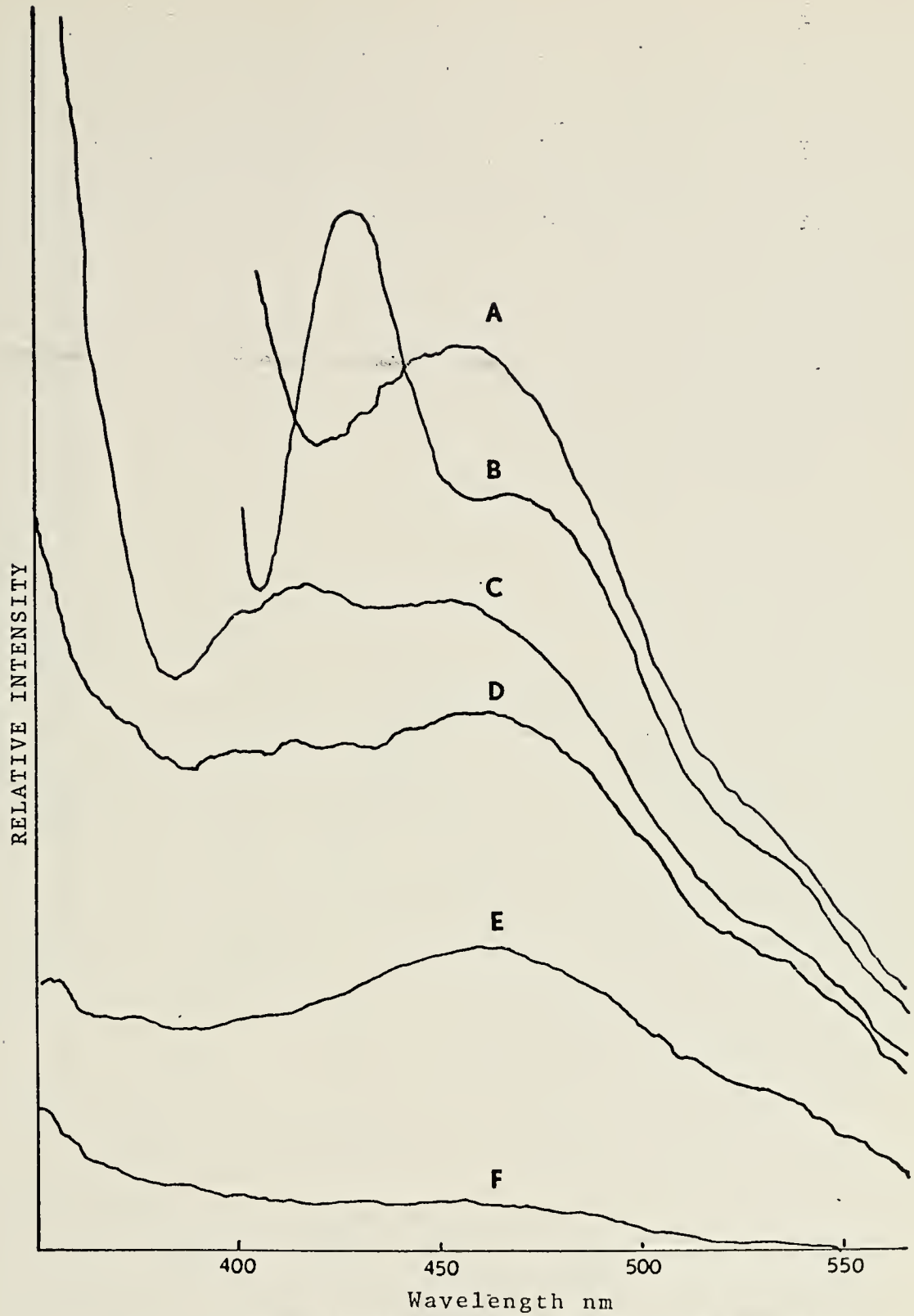

Fig. 16. Fluorescence spectra of a bottom sample of nonfiltered sea water from station two (Fig. 1). Excitations are: A, 340 nm; B, 370 nm; C, 310 nm; D, 290 nm; E, 250 nm; F, 220 nm.

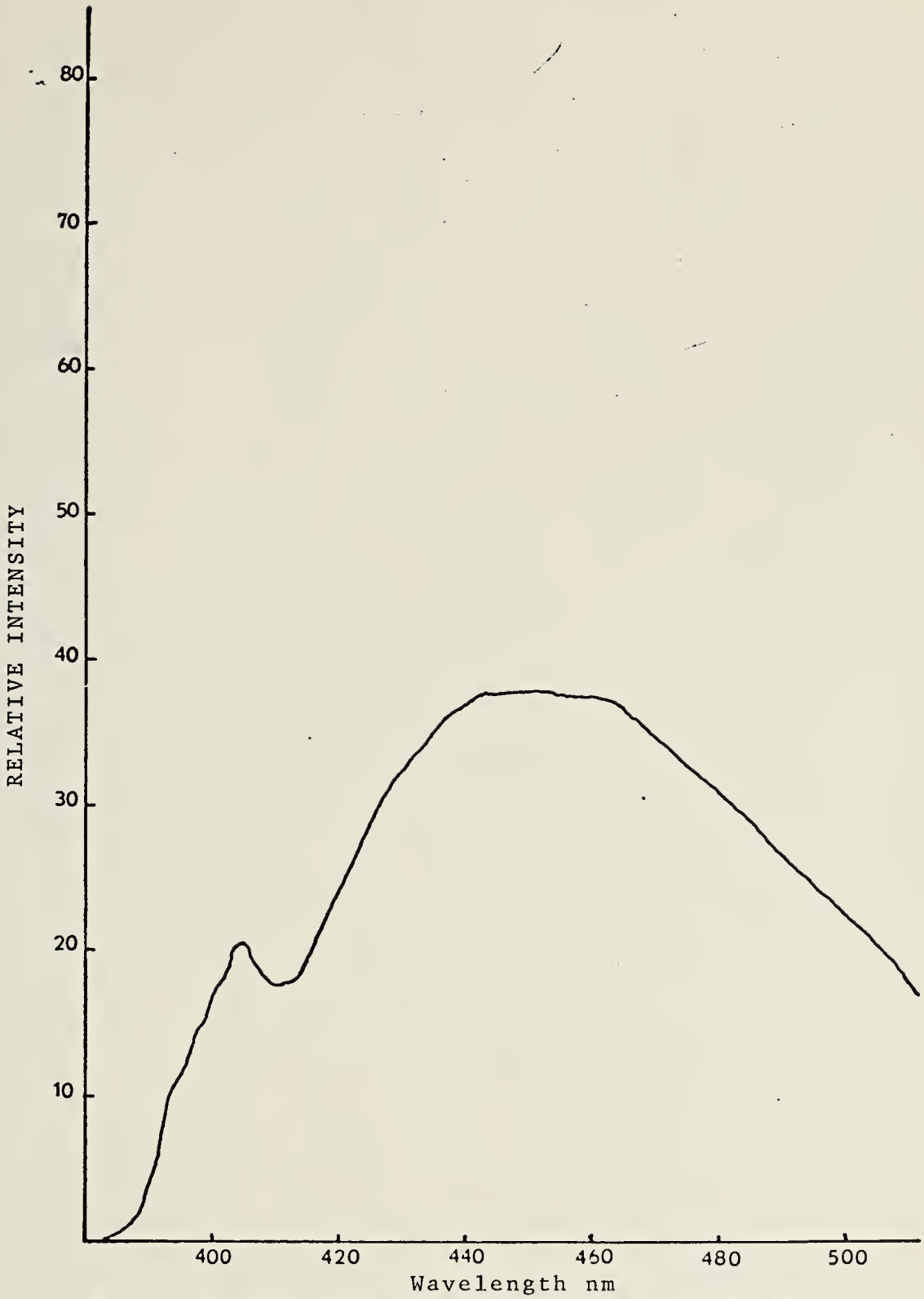

Fig. 17. Fluorescence spectra of a filtered surface sample of sea water from the Arctic Ocean, taken on Perkin-Elmer MPF2-A Fluorescence Spectrofluorometer.

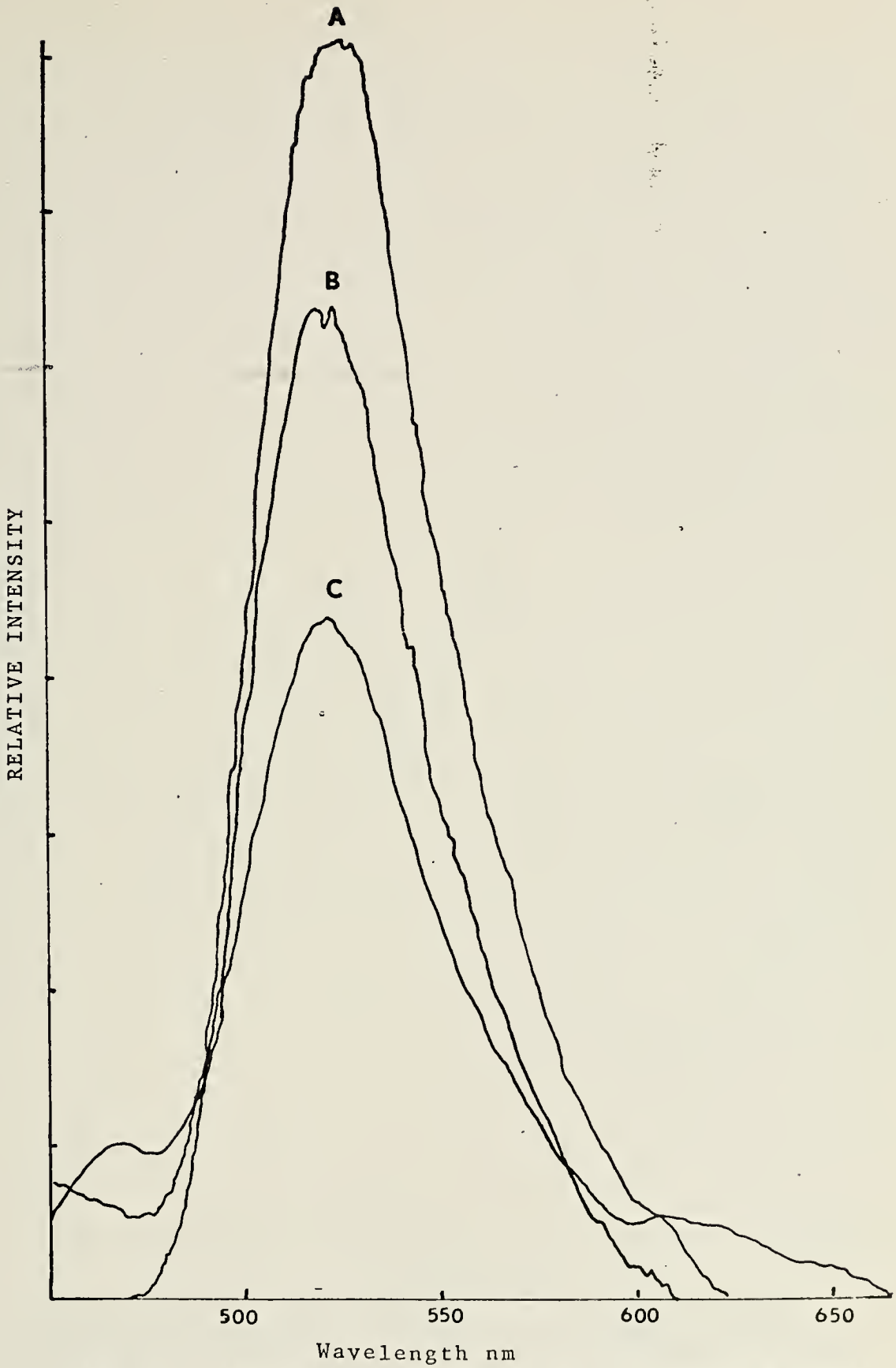

Fig. 18. Fluorescence spectra of a filtered surface sample of sea water from station two (Fig. 1). Excitations are: A, 300 nm; B, 250 nm; C, 400 nm.

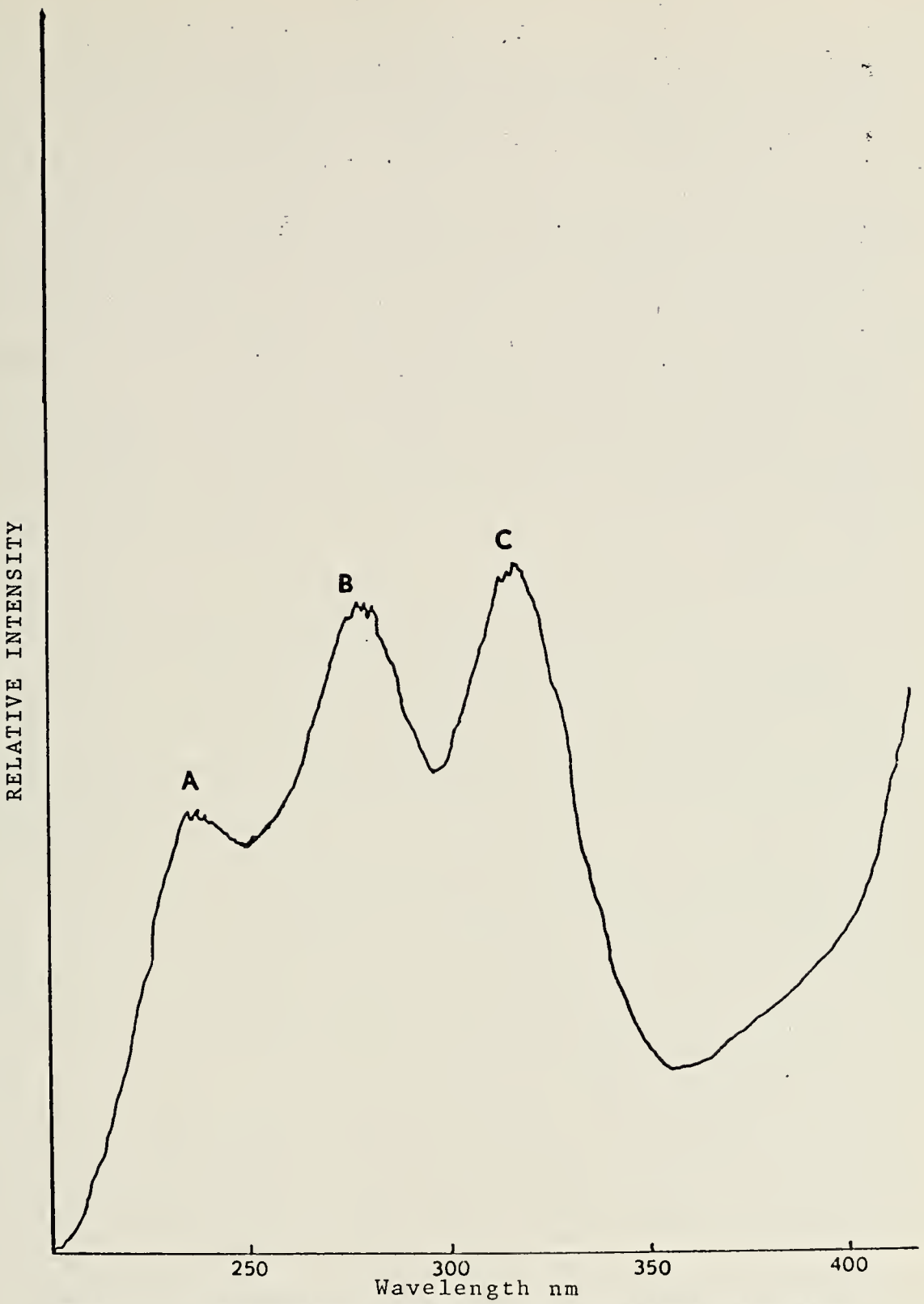

Fig. 19. Excitation spectra of a filtered surface sample of sea water from station two (Fig. 1). Excitation peaks are at: A, 230 nm; B, 280 nm; C, 320 nm.

The broad banded fluorescence centered at 450 nm may indicate the presence of a group of compounds in the samples.

The only exception observed to the general fluorescence emission observed at 450 nm was the fluorescence spectra of a filtered surface sample (Fig. 11) taken at station two (Fig. 1). The characteristic emission was at 520 nm when the sample was excited at 250 nm, 300 nm and 400 nm. The excitation spectrum showed maximum peaks at 230 nm, 280 nm and 320 nm (Fig. 19).

B. CHARACTERIZATION OF NAVAL FUEL OIL SAMPLES

Excitation and fluorescence spectra for the 5 Naval fuels in cyclohexane are shown in Fig. 20 and Fig. 27. The maximum excitation and fluorescence peaks for each fuel are summarized in Table 2.

The traces are characteristic to a degree which may permit direct identification, by passive fluorescence techniques against the natural fluorescence background.

Navy Distillate fuel has characteristic excitation peaks at 290 nm and 240 nm when the analyzing monochromator is set at 350 nm (Fig. 21). The fluorescence spectrum shows a maximum at 330 nm with a slight shoulder at 315 nm and a more prominent one at 340 nm (Fig. 20).

Navy Standard Fuel Oil has characteristic excitation peaks at 315 nm, 350 nm, and 400 nm when the analyzing monochromator is set at 450 nm (Fig. 33). When excited at 320 nm,

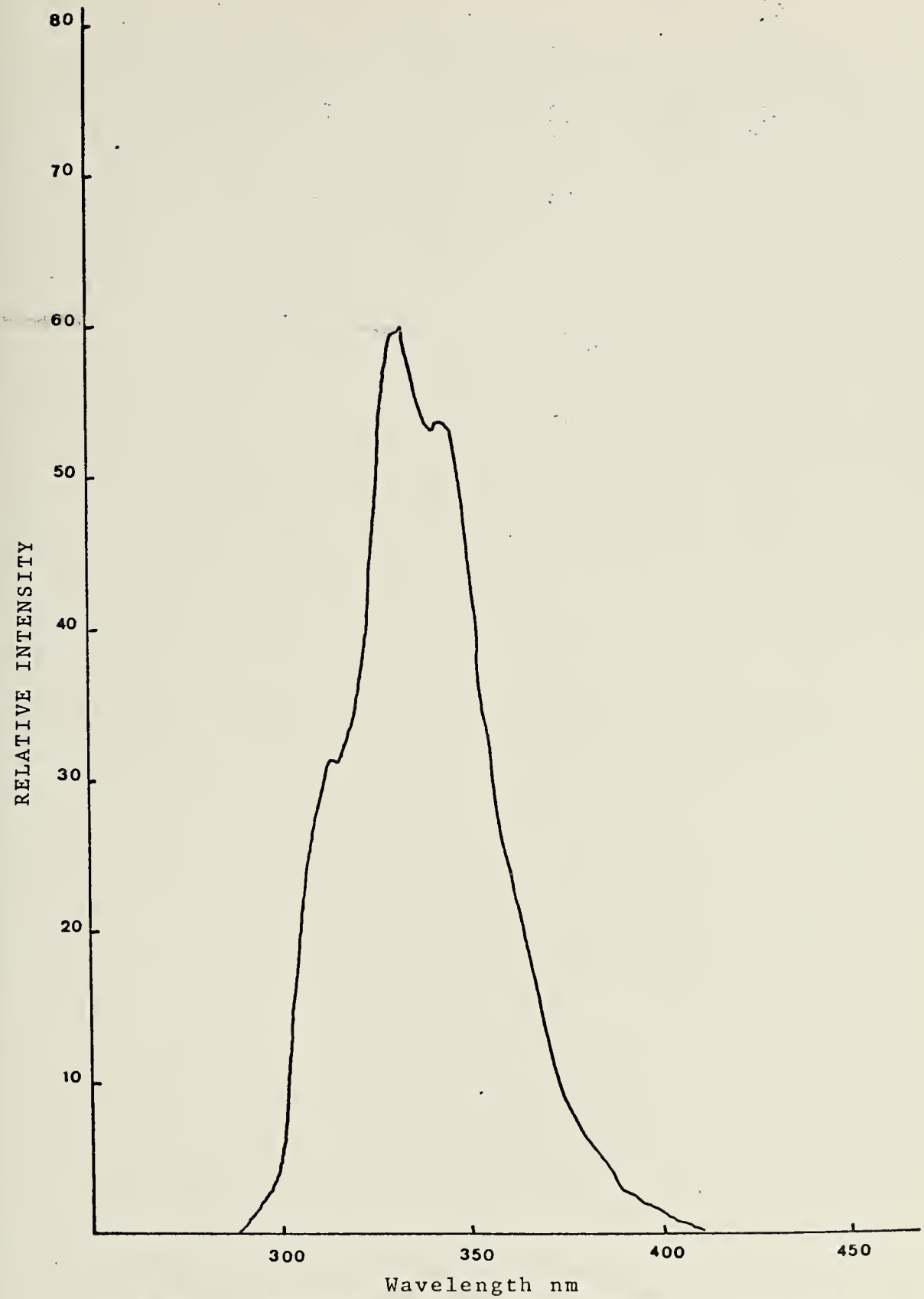

Fig. 20. Fluorescence spectrum of Navy Distillate Fuel (ND) in cyclohexane(10^4ng/ml)with excitation of 290 nm.

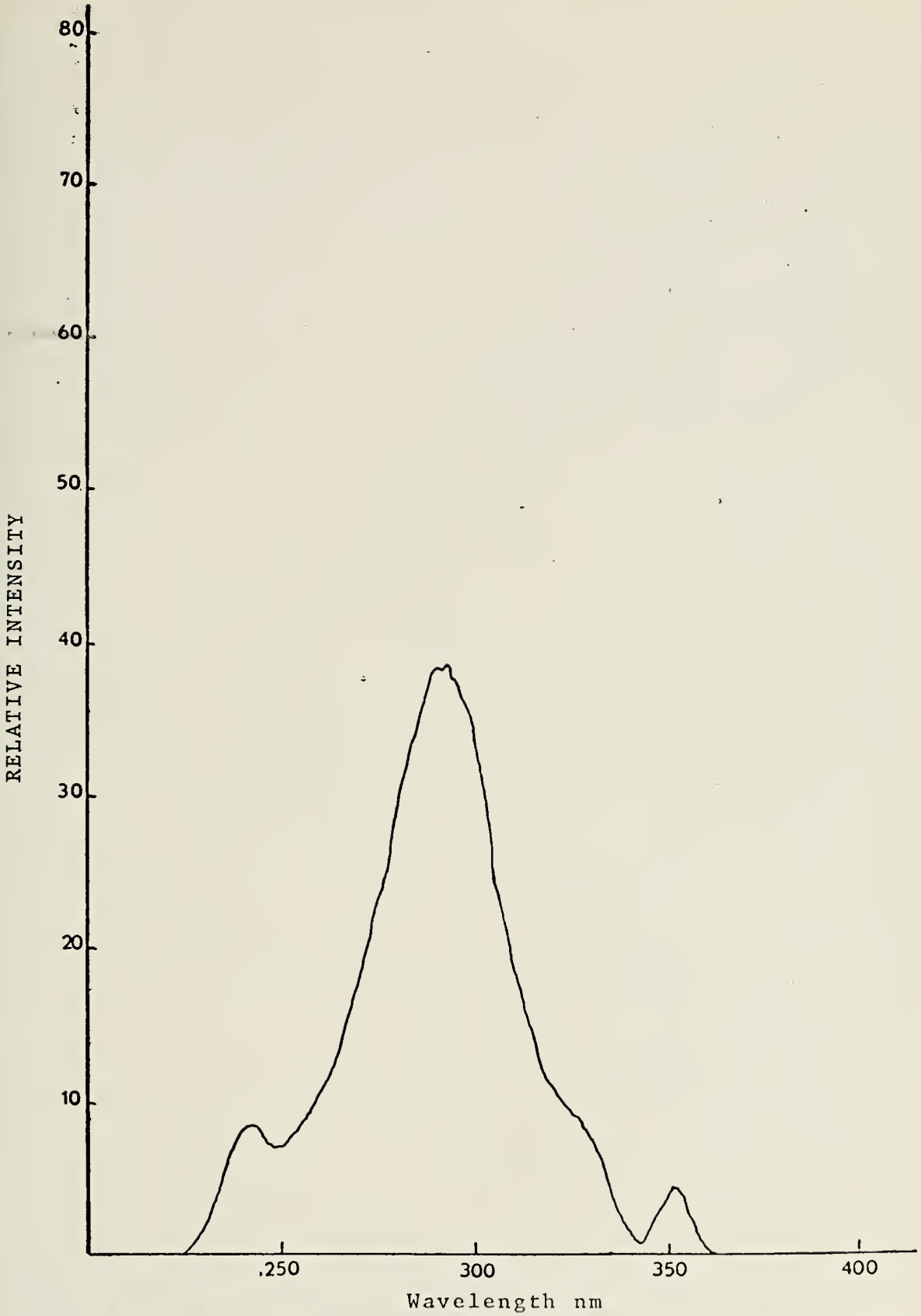

Fig. 21. Excitation spectra of Navy Distillate Fuel in cyclohexane (10^4ng/ml) with analyzing monochromator set at 340 nm.

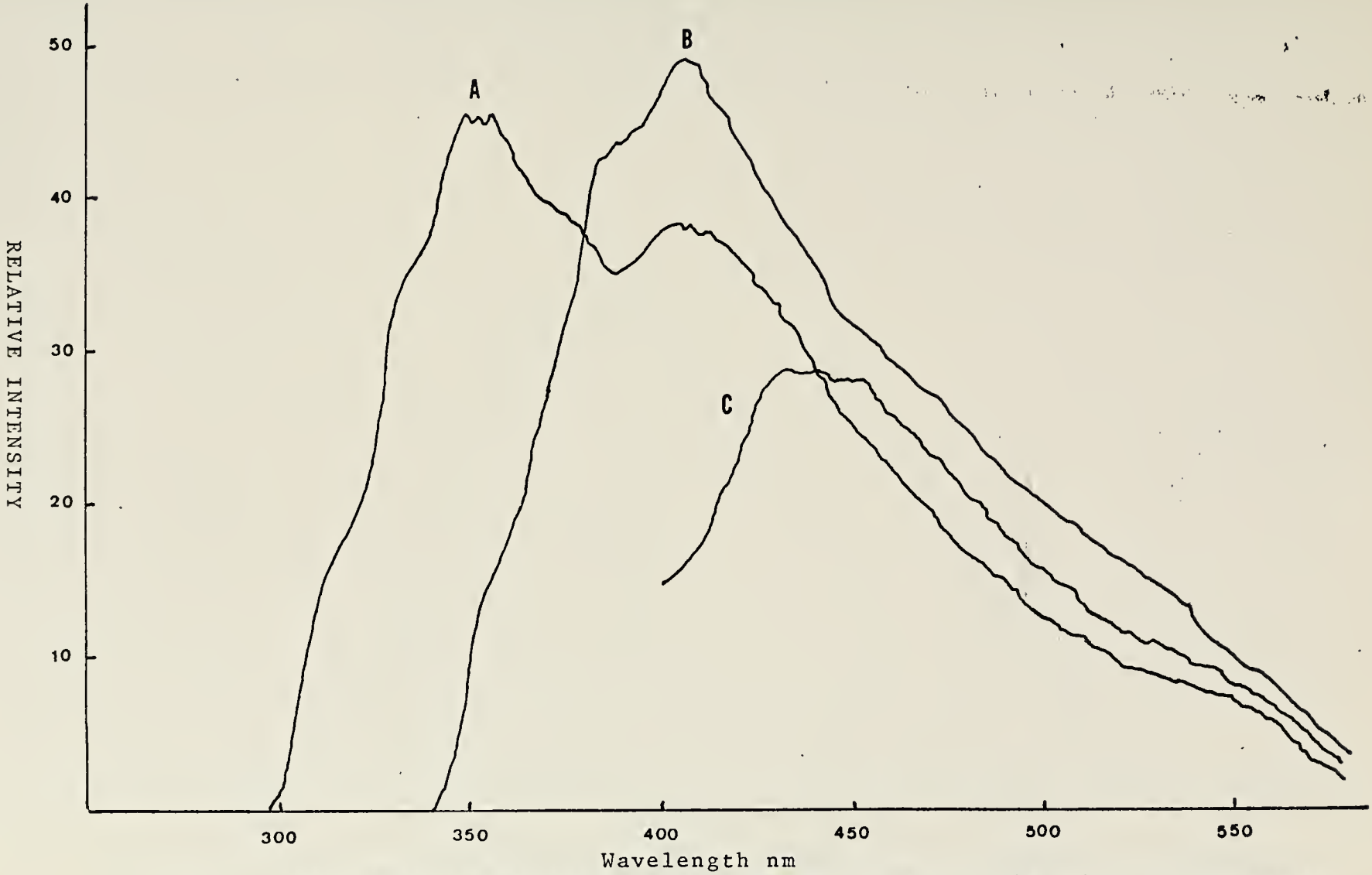

Fig. 22. Fluorescence spectra for Navy Standard Fuel Oil (NSFO) in cyclohexane (10^4ng/ml) A, excitation at 320 nm; B, excitation at 340 nm; C, exciation at 400 nm.

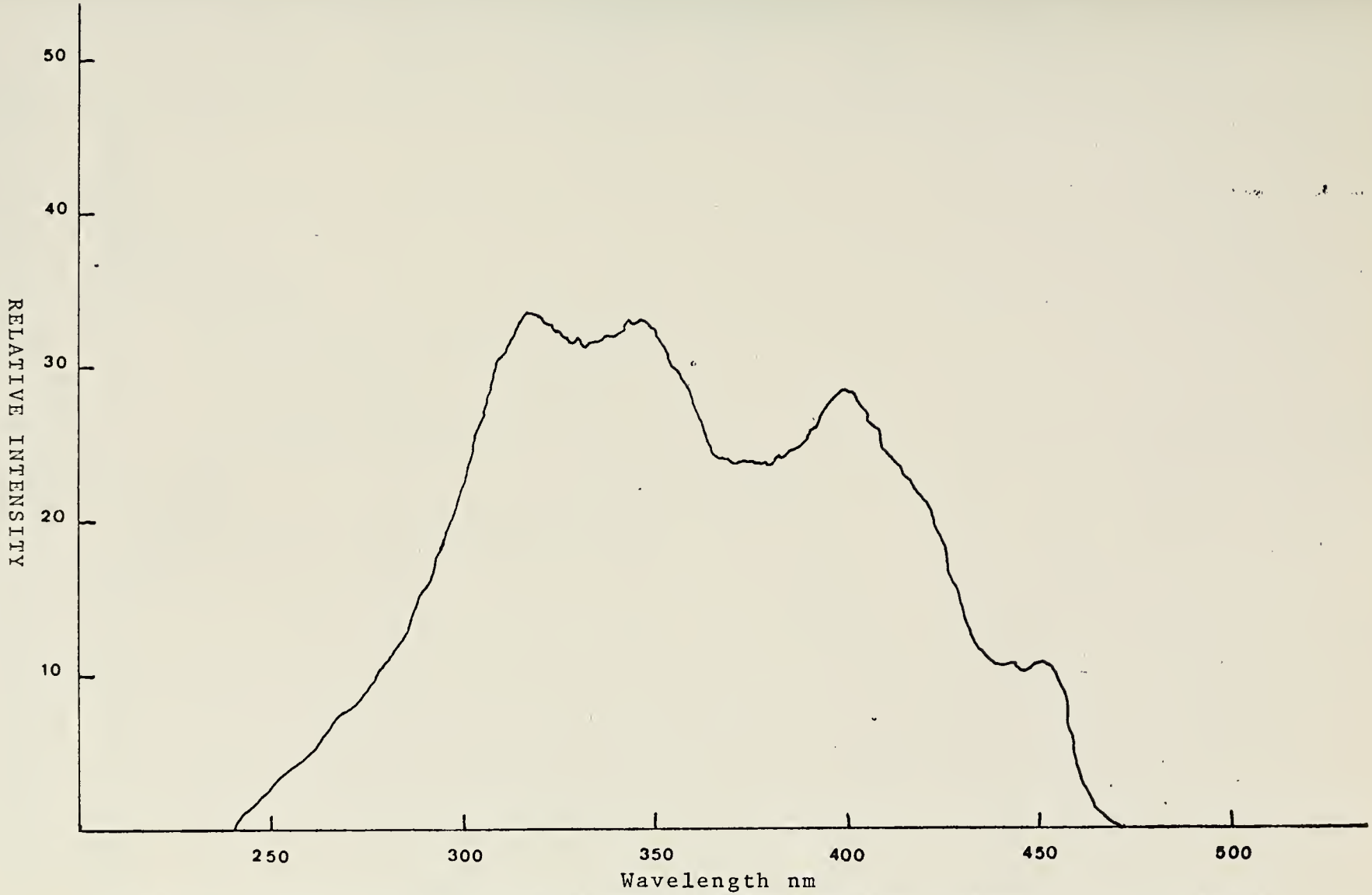

Fig. 23. Excitation spectrum of Navy Standard Fuel Oil (NSFO) in cyclohexane (10^4ng/ml) with analyzing monochromator set at 450 nm.

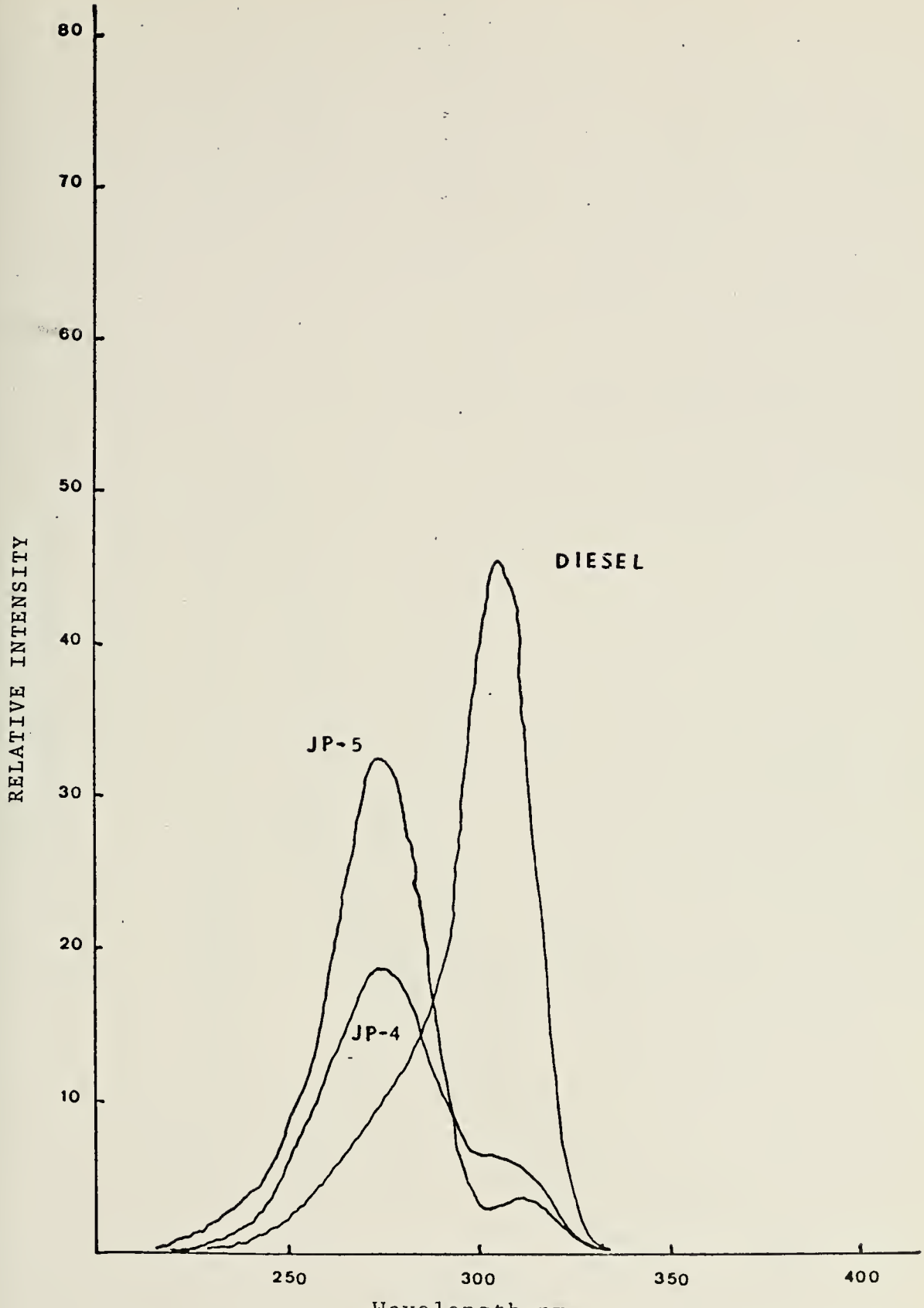

Fig. 24. Excitation spectra of JP-4, JP-5 and Diesel Fuel in cyclohexane (10^6ng/ml) with analyzing monochromator set at 310 nm.

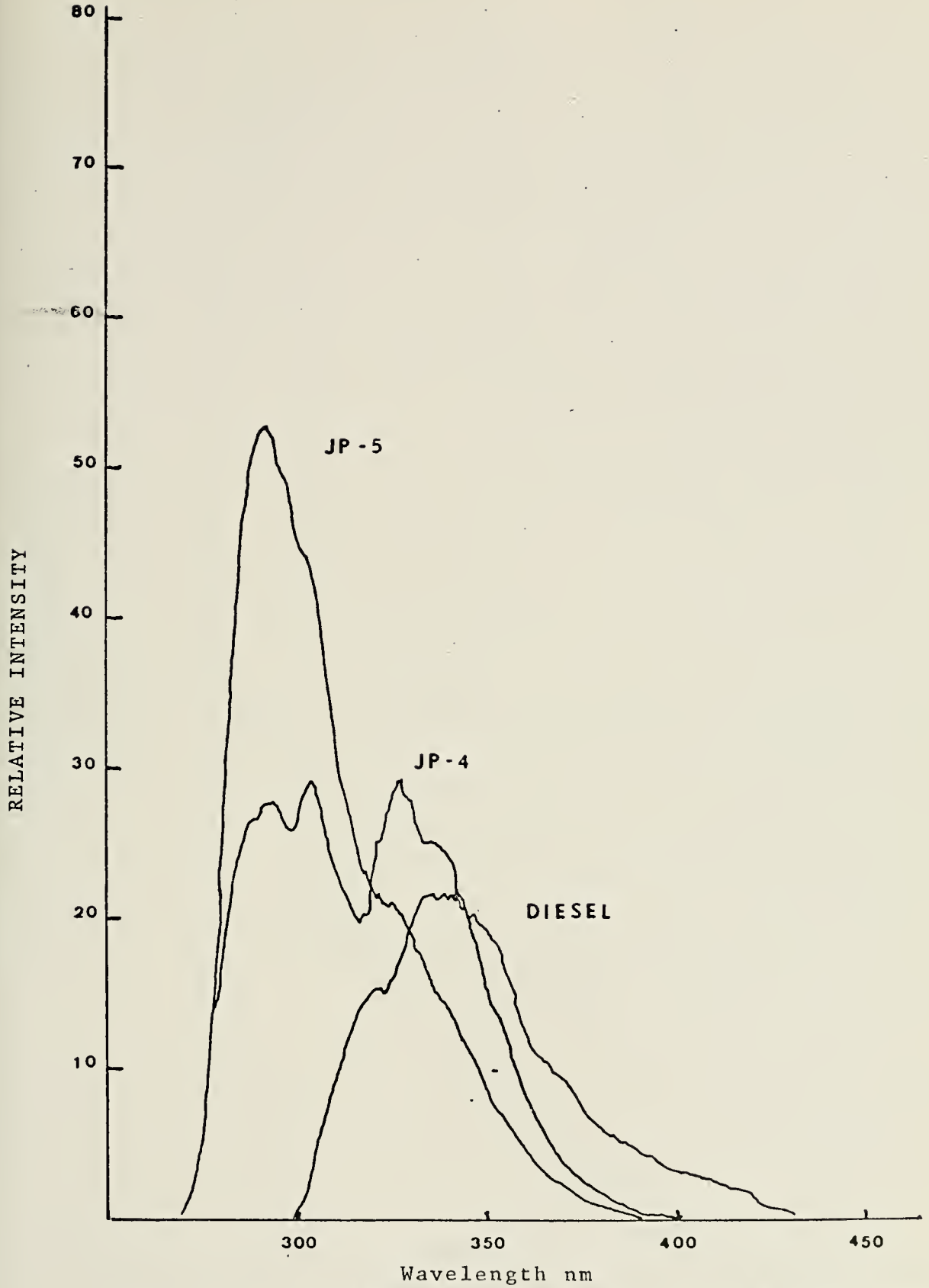

Fig. 25. Fluorescence spectra of JP-4, JP-5 and Diesel Fuel in cyclohexane (10^6 ng/ml) with excitation at 250 nm.

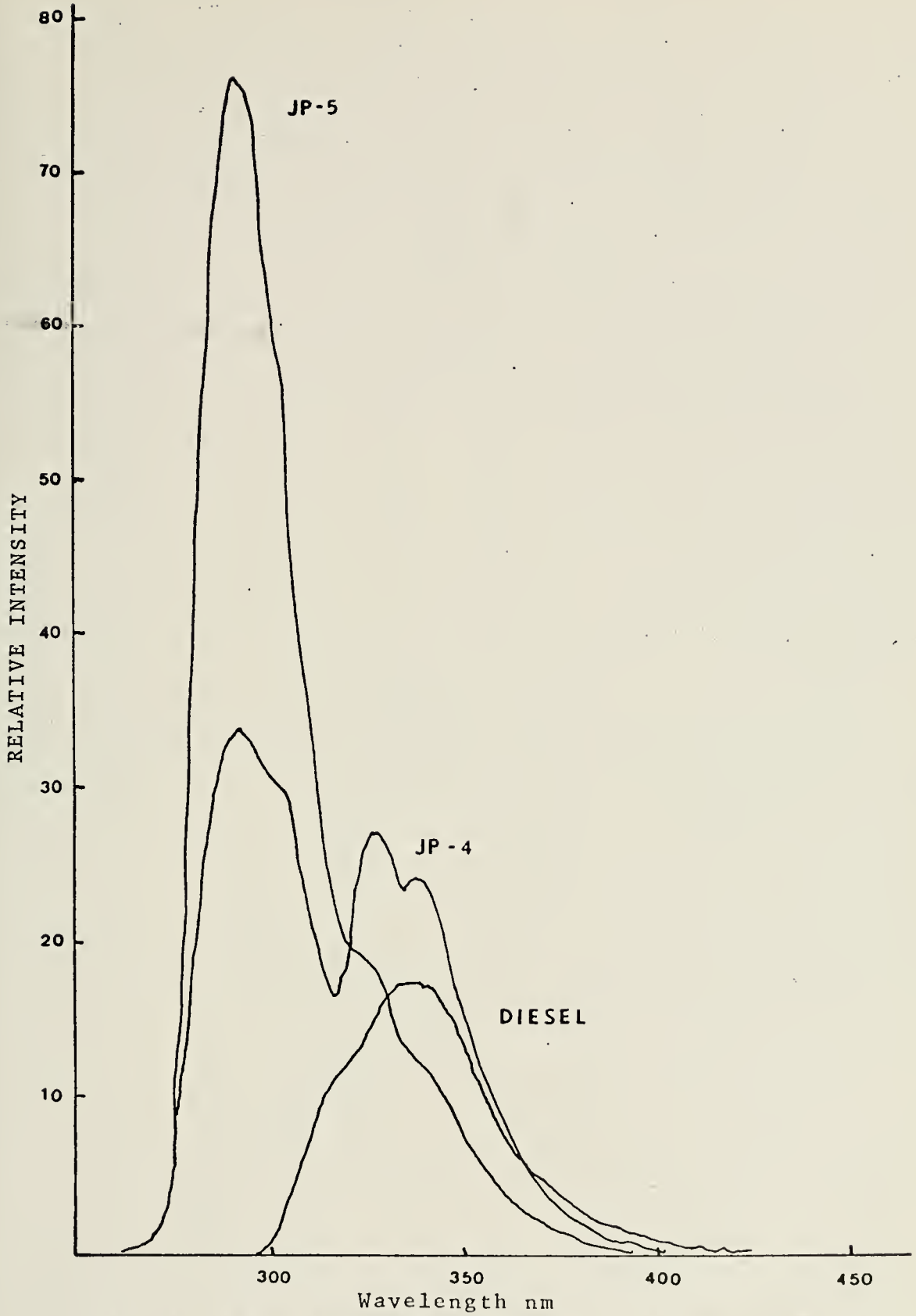

Fig. 26. Fluorescence spectra of JP-4, JP-5 and Diesel Fuel in cyclohexane (10^6ng/ml) with excitation at 270 nm.

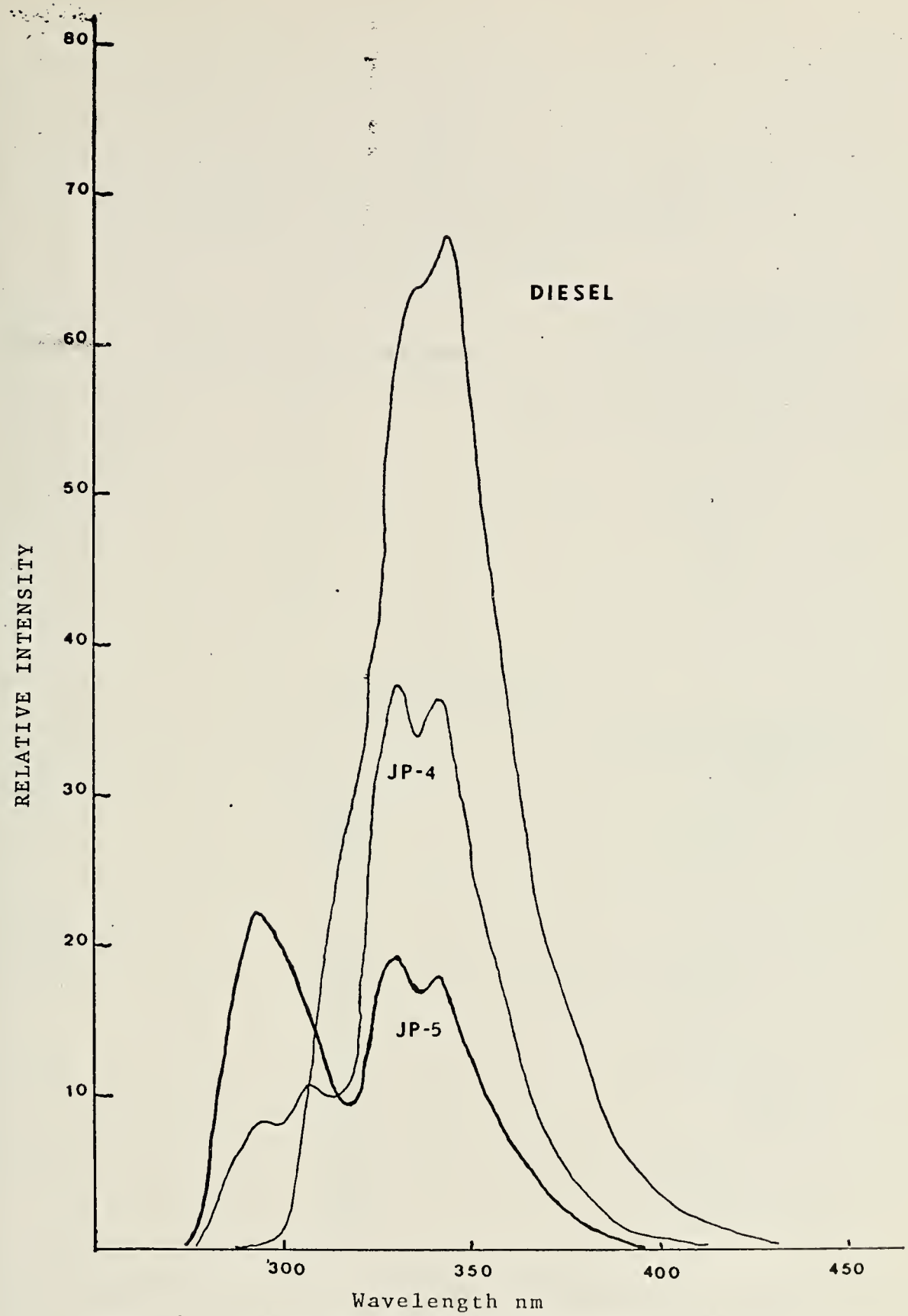

Fig. 27. Fluorescence spectra of JP-4, JP-5 and Diesel Fuel in cyclohexane (10^6ng/ml) with excitation at 280 nm.

TABLE 2

Characteristic Peak Fluorescence and Excitation for Five Naval Fuels in Cyclohexane

EXCITATION SPECTRA

Navy Fuel	Fluorescence Observed	Peak and/Shoulder Excitation
NSFO	450	320, 340, 400
Distillate	350	235, 290
Diesel	350/310	300/305
JP-4	310	275
JP-5	310	275

EMISSION SPECTRA

Sample	Excitation	Peak and/Shoulder Emission
NSFO	320	350, 410
	340	410
	400	450
Distillate	310	340/350
Diesel	250	340
	270	340
	280	340
JP-4	250	290, 325
	270	290, 325
	280	340
JP-5	250	290
	270	290
	280	290, 340

peak fluorescence was observed at 350 nm and 410 nm. When excited at 340 nm, the peak emission occurred at 410 nm with a slight shoulder at 385 nm. When excited at 400 nm, NSFO fluorescence was recorded at 450 nm (Fig. 22).

The excitation spectra for JP-4 and JP-5 shows peaks at 275 nm; however, their fluorescence spectra vary with excitation wavelength. Selectivity for these two fuels has been achieved by observing these variations for several excitation wavelengths (Fig. 25 through 27). Figure 25 shows fluorescence of JP-4 and JP-5 when excited at 250 nm. JP-5 has a prominent peak at 290 nm and a slight shoulder at 320 nm. JP-4 on the other hand, has two prominent peaks, one at 290 nm and one at 325 nm. When excited at 270 nm, intensity shifts were observed; however, JP-4 maintained two prominent peaks to JP-5's one (Fig. 26). When excited at 280 nm, a complete shift in peak intensities was observed with JP-5 now showing two prominent peaks at 290 nm and 340 nm against a single distinct peak for JP-4 at 340 nm with shoulders at 290 nm and 310 nm (Fig. 27).

Diesel fuel exhibits fluorescence at 340 nm when excited at all three of the wavelengths above (Fig. 25 through 27).

C. QUANTITATIVE DETERMINATION OF NAVY DISTILLATE FUEL OIL AT KNOWN PERCENT SATURATION IN SEA WATER

Figure 27 and 29 are fluorescence spectra of six samples of sea water contaminated with Navy Distillate Fuel. Figure 28 is before extraction and Figure 29 is after extraction with spectro quality cyclohexane.

Fig. 28. Fluorescence spectra of Navy Distillate Fuel in sea water before extraction with cyclohexane. Excitation is at 310 nm. A, 100% Sat.; B, 90% Sat.; C, 70% Sat.; D, 50% Sat.; E, 30% Sat.; F, 10% Sat.

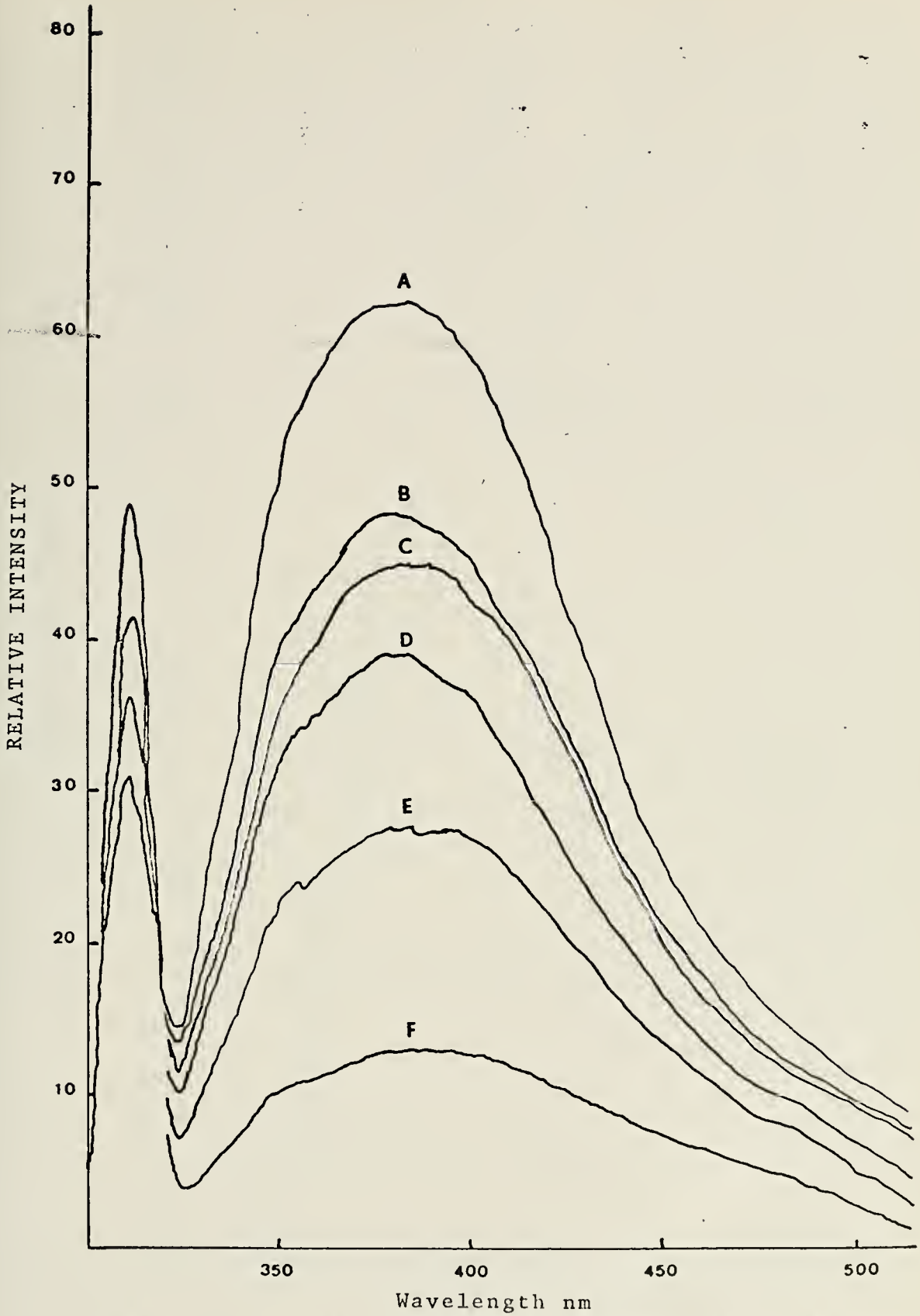

Fig. 29. Fluorescence spectra of Navy Distillate fuel in sea water after extraction with cyclohexane. Excitation is at 310 nm. A, 100% Saturation; B, 90% Sat.; C, 70% Sat.; D, 50% Sat.; E, 30% Sat.; F, 10% Sat.

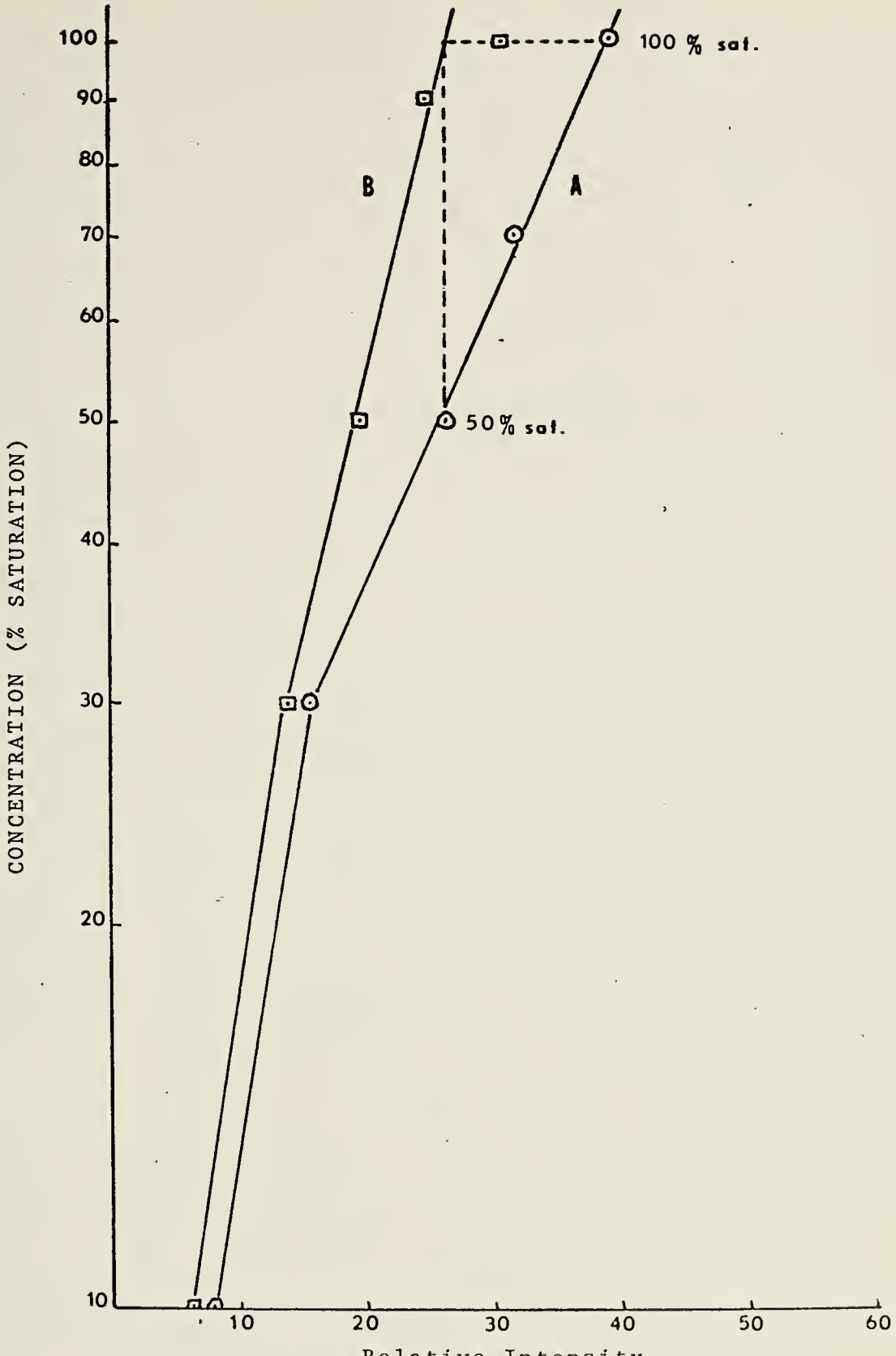

Fig. 30. Fluorescence intensity of ND in sea water vs concentration. A, before extraction; B, after extraction.

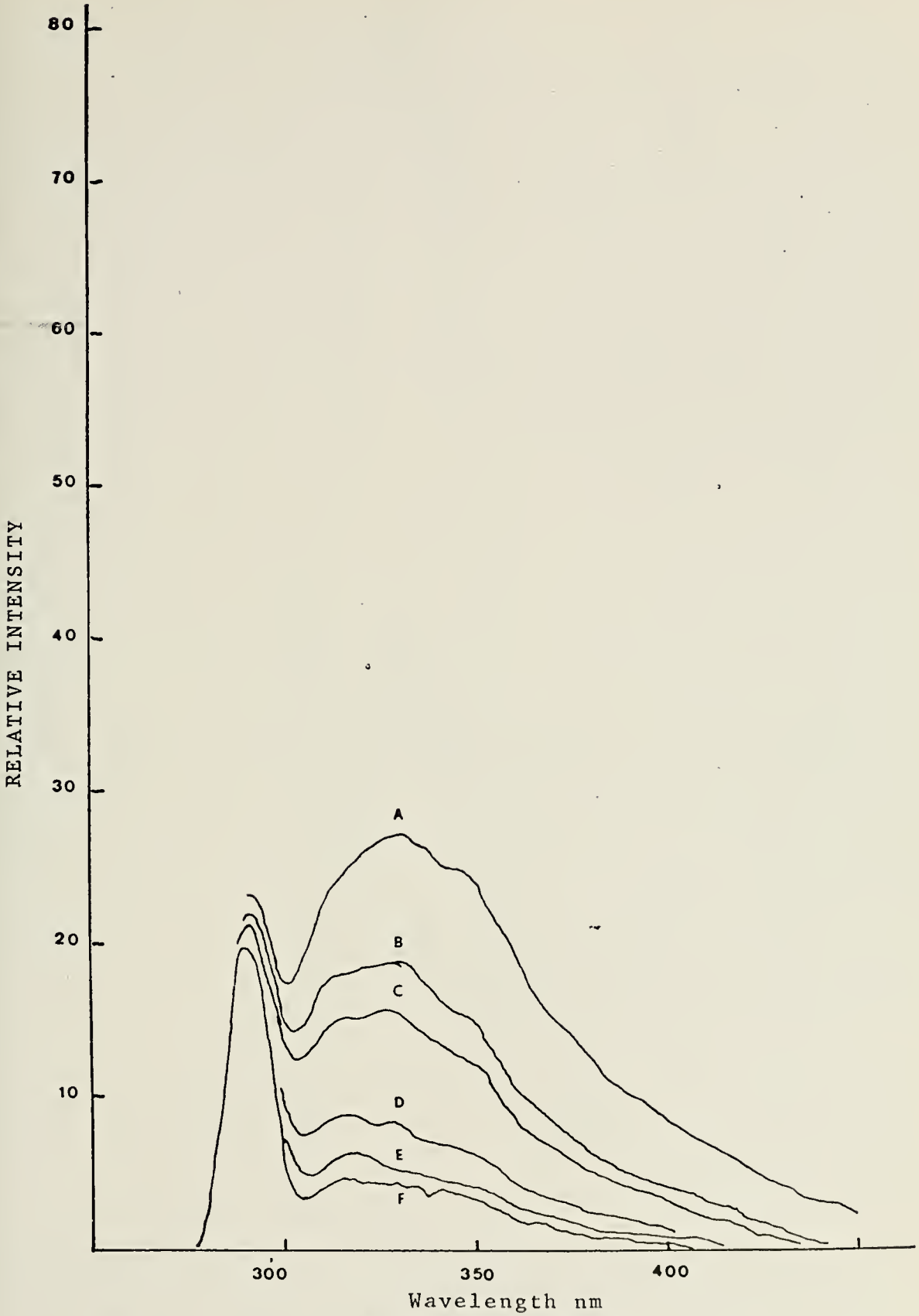

Fig. 31. Fluorescence of Navy Distillate Fuel in Cyclohexane extract. Excitation is at 290 nm. Curva A represents the fluorescence of the extract from a 100% saturated sample of ND in sea water; B, 90% Sat.; C, 70% Sat.; D, 50% Sat.; E, 30% Sat.; F, 10% Sat.

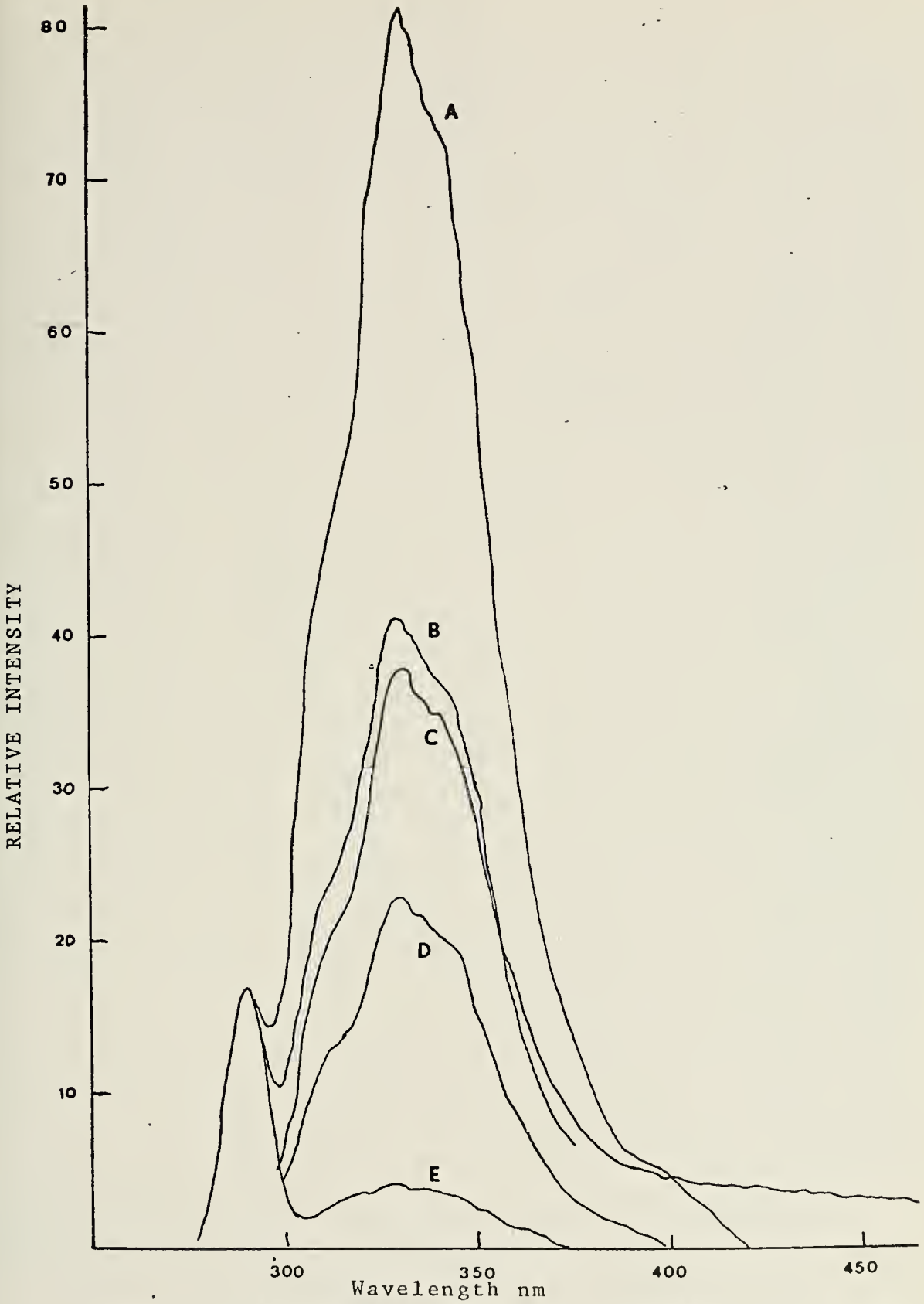

Fig. 32. Standardization fluorescence spectra for ND in cyclohexane at excitation 290 nm. A, $2x10^4$ng/ml; B, 10^4ng/ml; C, $5x10^4$ng/ml at lower sensitivity; D, $2x10^4$ng/ml at lower sensitivity; E, 10^3ng/ml.

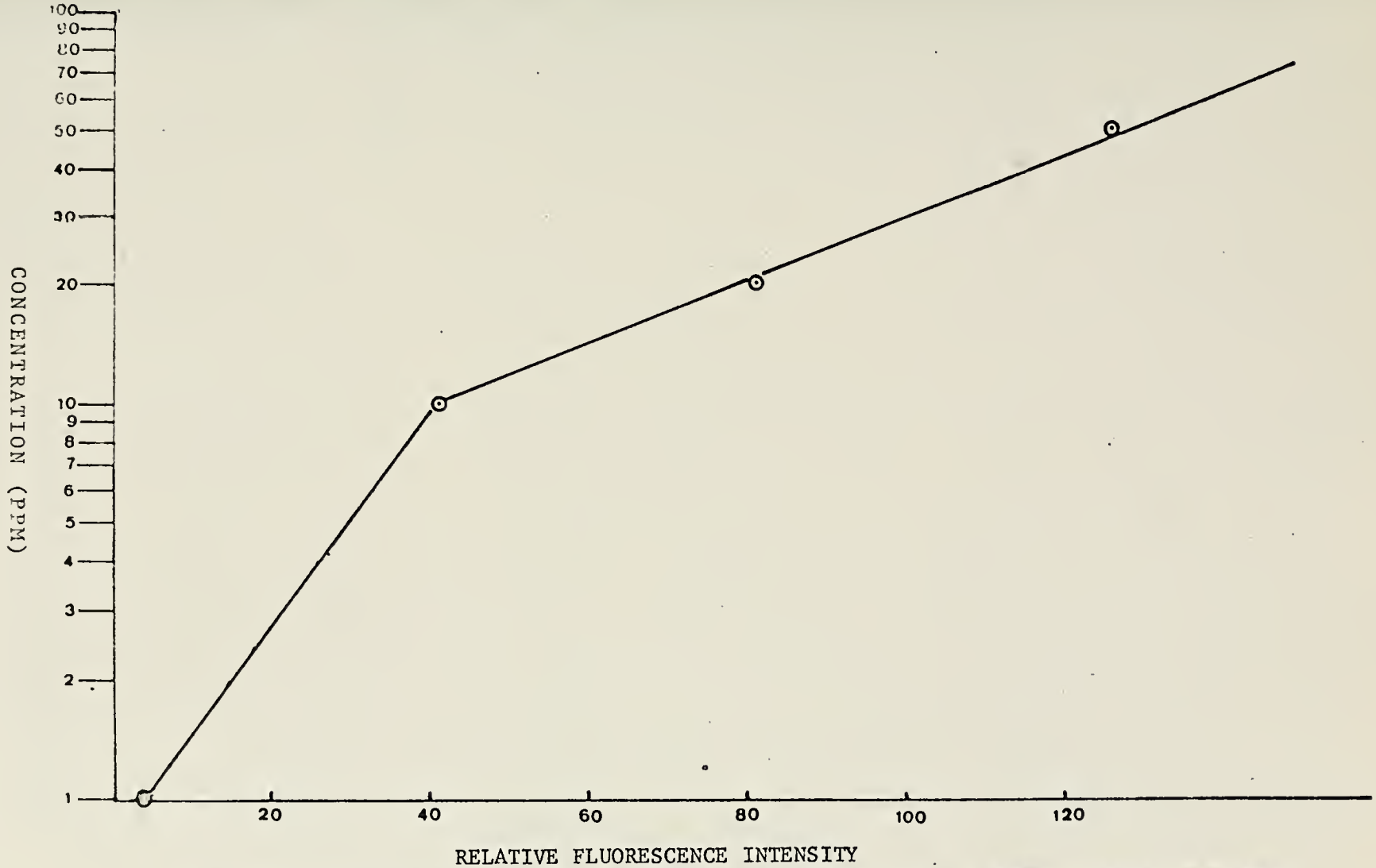

Fig. 33. Standard curve for known concentrations of Navy Distillate Fuel in "Spectroquality" cyclohexane (1.0 ppm = 10^3ng/ml).

Figure 30 is a semi log plot of concentration versus intensity of fluorescence. The discontinuity at 30% saturated is supported by data points from previous runs at concentrations below 10% saturated. The fluorescence of the 100% saturated sample after extraction shows a drop in concentration of ND to 50% saturation. The apparent equilibrium coefficient is 1.0 for the extraction process. Figure 31 shows the fluorescence spectra of the extract of each level of saturation. Figure 32 is the fluorescence spectra for known concentrations of Navy Distillate fuel in cyclohexane. A standard curve for fluorescence of Navy Distillate in cyclohexane is plotted in Figure 33. The average drop in Navy Distillate for Figure 30 is 40%, leaving 60% in the water. This gives an equilibrium coefficient for the extraction of 1.5.

The data indicates that the 100% saturated sample of ND in sea water contains approximately 11 ppm (11×10^3 ng/ml) Navy Distillate fuel.

D. PRECISION

The instrument precision of the Turner 210, utilized throughout this study, is given in Table 3 as a standard deviation, computed from 20 relative fluorescence intensities for two different excitation wavelengths. When exciting quinine bisulfate at 350 nm, the standard deviation in relative intensity units is 1.56 intensity units. The standard deviation for excitations at 250 nm is 1.53 intensity units.

TABLE 3

Standard Deviation Results for Precision Equipment Using Replicate Fluorescence Spectra for 10 ppm (10^4ng/ml) quinine bisulfate in 0.1N Sulfuric Acid

Run	Time hrs/min	Relative Fluorescence Intensity (at 400 nm) (excitation at 350 nm)	Relative Fluorescence Intensity (at 460 nm) (excitation at 250 nm)
1	00	77	60
2	15	82	65
3	30	81	65
4	45	80	64
5	1:00	79	61
6	15	80	62
7	30	80	62
8	45	79	61
9	2:00	83	62
10	15	82	61
11	30	82	63
12	45	81	64
13	3:00	80	64
14	15	79	61
15	30	82	64
16	45	83	61
17	4:00	83	63
18	15	80	62
19	30	81	63
20	45	82	65

Standard Deviation (σ)

σ (excitation at 250 nm) = $\pm$ 1.53 intensity units
σ (excitation at 350 nm) = $\pm$ 1.56 intensity units

Relative Standard Deviation (RSD) $\left(\frac{\text{avg.}}{\sigma} \times 100\right)$

RSD (excitation at 250 nm) = 1.90 percent
RSD (excitation at 350 nm) = 1.93 percent

TABLE 4

Fluorescence of 50% and 5% Saturated ND in Sea Water Before and After Extraction with Cyclohexane

Sample	Fluorescent Intensity (at 380 nm) (excitation at 290 nm)	
	Before Extraction	After Extraction
50% Sat.		
1	87	76
2	93	80
3	90	79
5.0% Sat.		
1	19	15
2	14	10
3	16	10

Standard Deviation (σ)

σ_1 (50% Sat. before extraction) = $\pm$ 2.45 intensity units
σ_2 (50% Sat. after extraction) = $\pm$ 1.90 intensity units
σ_3 (5% Sat. before extraction) = $\pm$ 2.05 intensity units
σ_4 (5% Sat. after extraction) = $\pm$ 2.32 intensity units

Relative Standard Deviation (RSD), $(\frac{avg}{\sigma} \times 100)$

RSD (σ_1) = 2.72 percent
RSD (σ_2) = 2.42 percent
RSD (σ_3) =12.5 percent
RSD (σ_4) =19.5 percent

The precision of extraction is evaluated in Table 1 at two concentration levels. The fluorescence intensity of three separate samples at 5 and 50% saturated ND in sea water yield a standard deviation in relative intensity units of $\pm$ 2.18 intensity units.

E. SENSITIVITY

Figures 34 and 35 show fluorescence spectra for three concentrations of Navy Distillate in cyclohexane, 10 ng/ml (10 ppb),1.0 ng/ml (1 ppb), 0.1 ng/ml (0.1 ppb). Fig. 36 shows fluorescence spectra for four different levels of saturation of samples of ND in seawater, (50% saturation, 5% saturation,0.5% saturation,0.05% saturation,0.005% saturation), (i.e. 5.5×10^{3}, 5.5×10^{2}, 5.5×10^{1}, 5.5×10^{-1} ng/ml).

Since the instrument was set in its most sensitive mode of operation, these concentrations represent the limits of detection for this method.

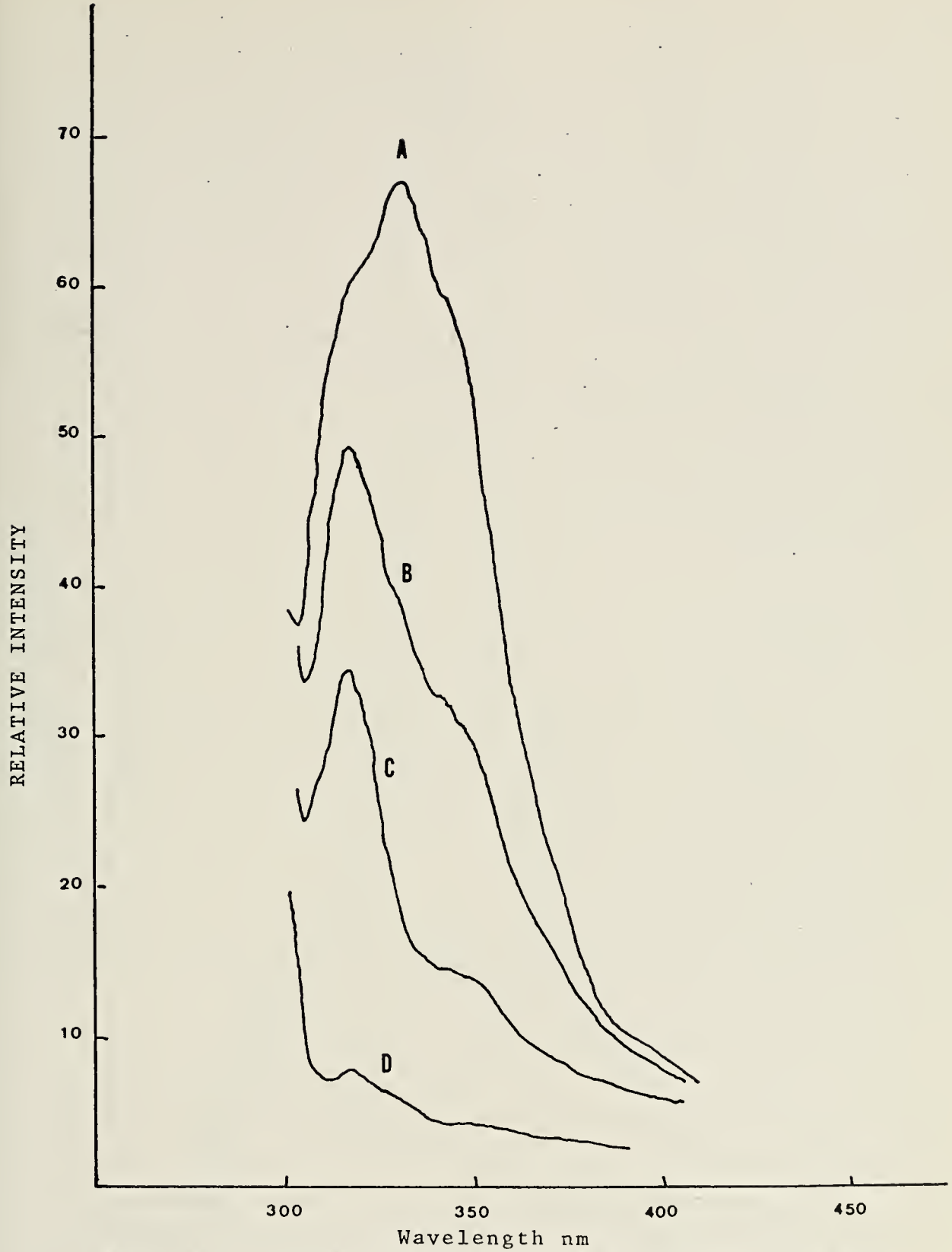

Fig. 34. Fluorescence spectra of Navy Distillate Fuel (ND) in cyclohexane at excitation 310 nm. A, 10^2ng/ml; B, 10 ng/ml; C, 1.0 ng/ml; D, 0.1 ng/ml.

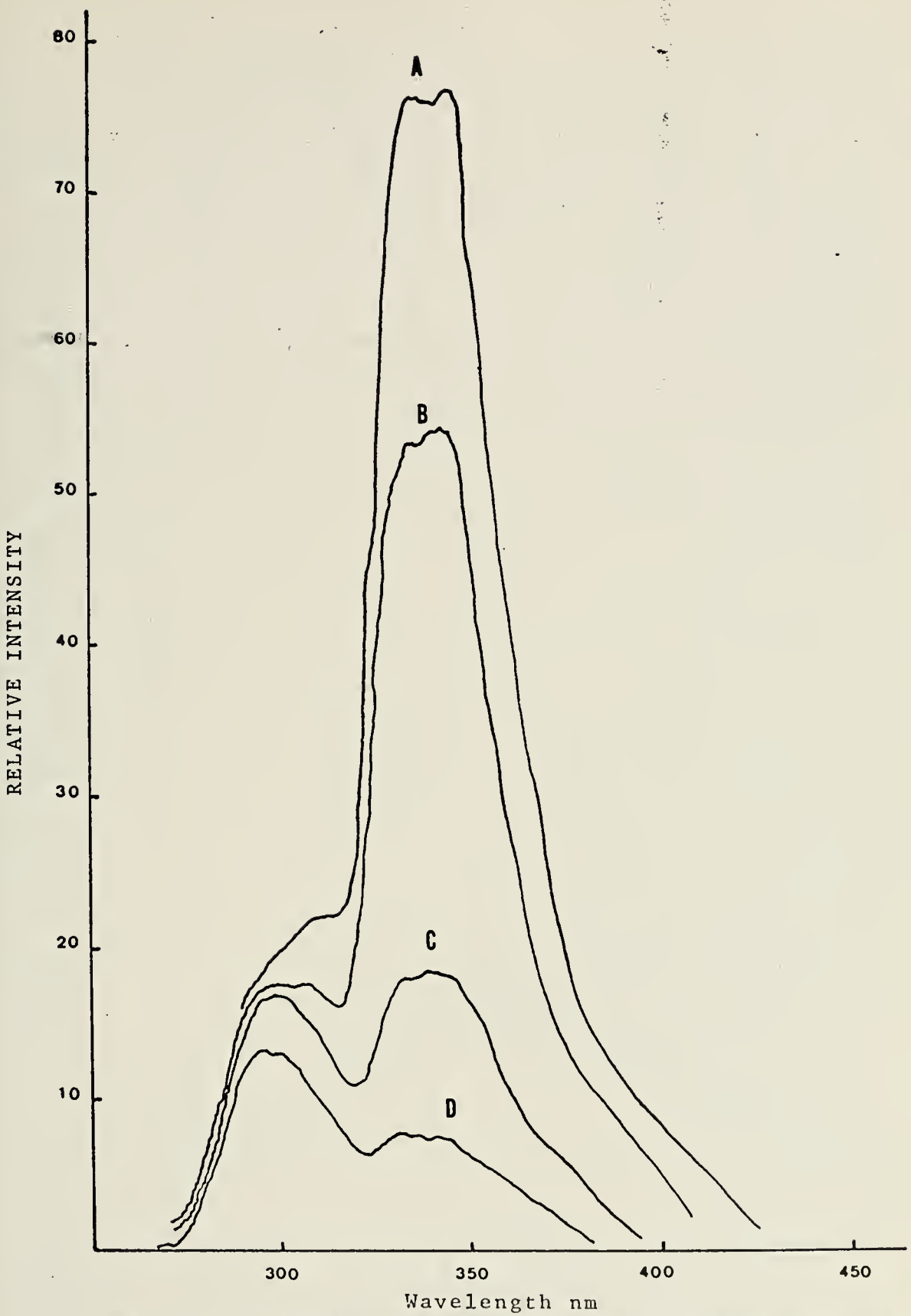

Fig. 35. Fluorescence spectra of Navy Distillate Fuel (ND) in cyclohexane at excitation 290 nm. A, 10^2ng/ml; B, 10 ng/ml; C, 1.0 ng/ml; D, 0.1 ng/ml.

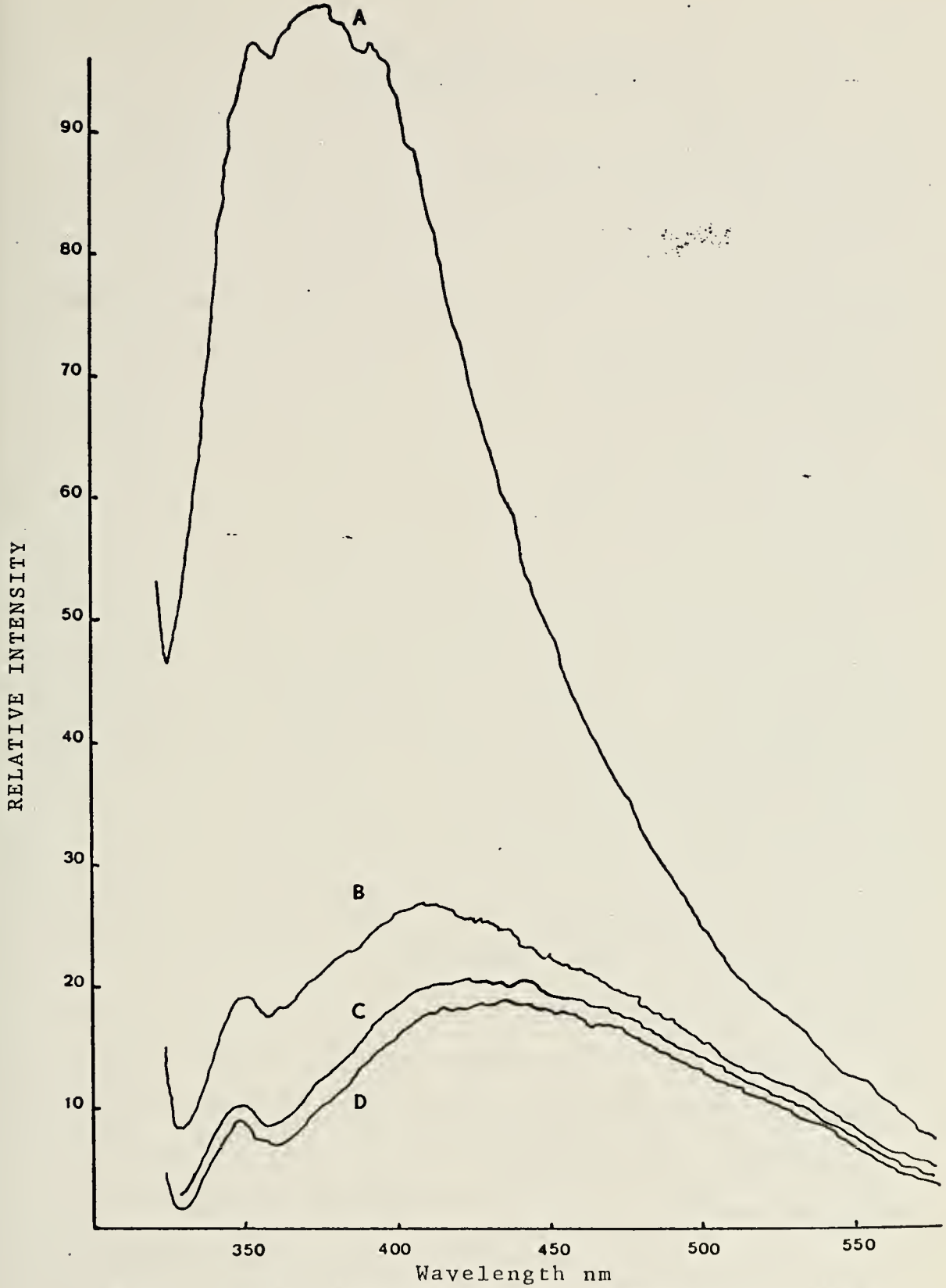

Fig. 36. Fluorescence spectra of Navy Distillate Fuel in sea water at excitation 310 nm. A, 5% Saturated; B, 0.5% Sat.; C, 0.05% Sat.; D, 0.005% Sat.

V. DISCUSSION OF RESULTS

The background natural fluorescence established for the Monterey Bay region suggests that the natural fluorescence found by others [Traganza 1967; Kalle 1966; Shtegman 1966] is "typical" of sea water in general, i.e. low concentration in the wave band 350 nm to 500 nm. The fluorescence of Arctic water (emission 400 nm to 450 nm) gives further evidence in support of this observation. It appears that on the average, the natural fluorescence background should not interfere with the fluorescence analysis of sea water for fuel oil contamination. This conclusion is supported by the relatively low instrumental sensitivity settings required for fuel oil determination in this study. Interference may occur if concentrations of some fuel oils are as low as 1.0 ng/ml or during biological events which can cause a transient "blackout" with blank values so high that fuels fluorescing in the same wavelength region will be masked.

Naval fuels were selectively identified at very low concentrations using passive fluorescence analysis of oil "fingerprints." Each Navy fuel was found to have characteristic fluorescence spectra (Fig. 20 through 27). For example, JP-4, JP-5 and Diesel were identifiable on the fluorometer but not separable by gas chromatography in another study in progress at this laboratory.

Table 5 is a summary of fluorescence characteristics reported for petroleum and various petroleum products. Riecker 1962, Shtegman 1966 and Smith 1968 have determined that various fuel oils fluoresce in the region from 440 to 630 nm. The only naval fuel which fluoresced in this region was NSFO which had a characteristic peak at 450 nm when excited at 400 nm (Fig. 22).

Parker and Barnes (1960) pointed out that fluorescence of hydrocarbons present in a sample, represents the cumulative fluorescence of a complex mixture and the lighter the fraction, the shorter the wavelength of fluorescence. This may explain the decreasing wavelengths observed for fluorescence of Diesel Fuel, JP-4 and JP-5 (Fig. 25 through 27).

Diesel Fuel was found to be well separated from JP-4 and JP-5; however, JP-4 and JP-5 fluoresce in the same band of wavelengths (Fig. 25 through 27). Selectivity was achieved between JP-4 and JP-5 by obtaining several fluorescence spectra at a variety of exciting wavelengths and comparing them. It is clear that the emission spectra are not similar for both JP-4 and JP-5 whereas their excitation spectra are (Fig. 25). Thus, we may assume the presence of more than one molecular species or reactive groups, which are fluorescent. With this variable excitation technique which can produce a separation in characteristic spectra, fluorescence spectra and excitation spectra either singly or together will provide selective identification of the Navy fuels examined.

Figure 37 shows the characteristic curve obtained for Kuwait Crude Oil and phytoplankton after the Torrey Canyon oil spill [Parker, et al. 1970]. The emission peak at 360 nm and shoulder at 400 nm are in the general region of NSFO emissions (Fig. 22). The fluorescence of the plankton suggests an uptake of crude oil by phytoplankton; however, the fluorescence was not unambiguously identified as due to crude oil.

Good instrumental sensitivity was achieved allowing detection down to 0.1 ng/ml of sea water (0.1 ppb). Parker and Barnes (1960) reported sensitivities from 0.2 ng/ml to 0.3 ng/ml (0.2 to 0.3 ppb) and suggest that the fluorescence blank from the cyclohexane solvent used may have been the limiting factor. For this reason, spectroscopically pure cyclohexane was used in this study with a slight increase in sensitivity to 0.1 ppb.

There was no observed Raman emission interference from the cyclohexane solvent in this study. This may be explained by the relatively high concentration level of the fluorescent material after extracting, which allowed fluorescence analysis to be done at instrumental sensitivities too low to be affected by Raman emissions.

Due to optimizing instrumental slit width and other sensitivity settings, to achieve high resolution and characteristic spectra for each fuel, this author feels that the overall method sensitivity, while superior to most techniques is "instrument limited" [Parker 1968] only to the

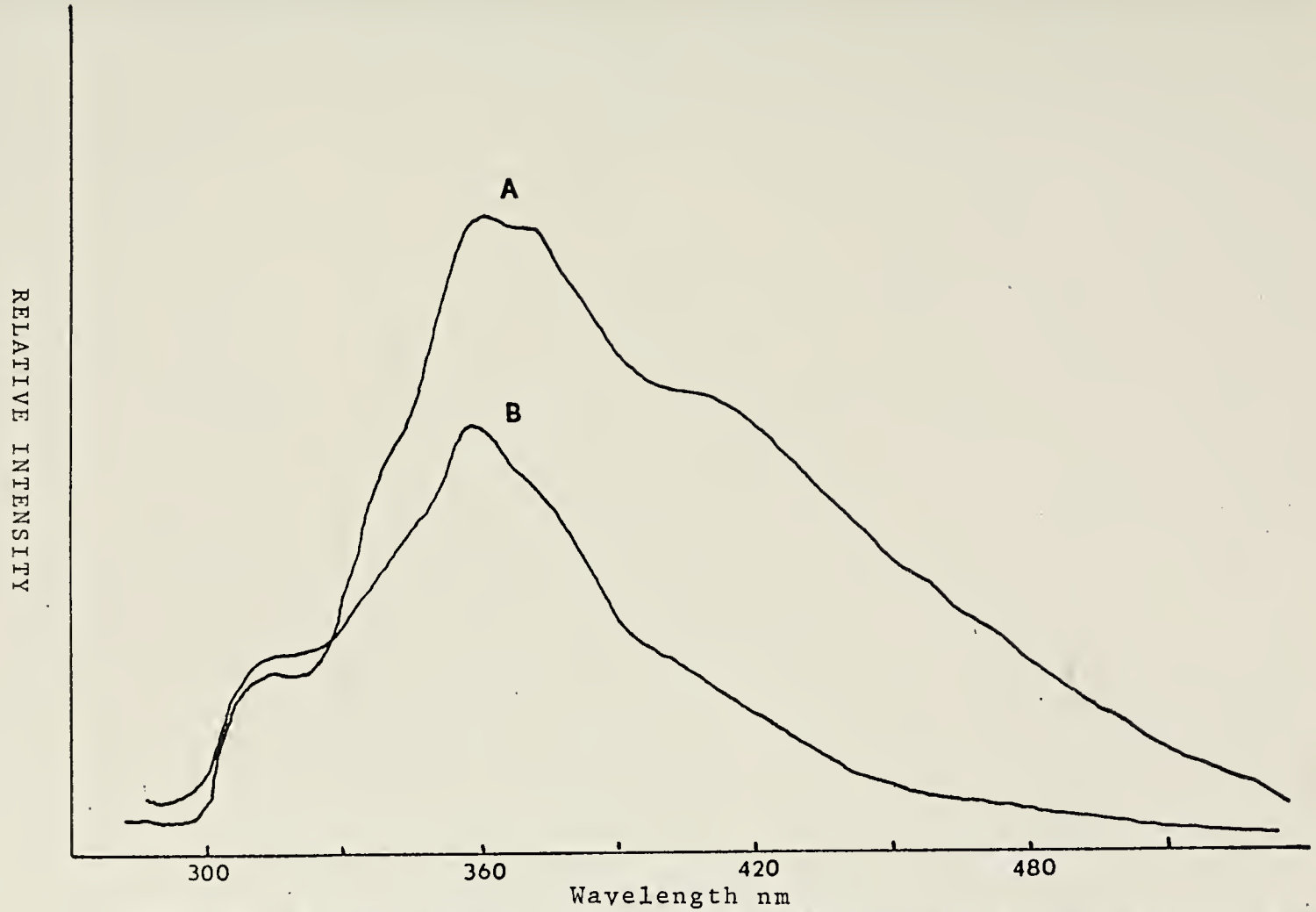

Fig. 37. [from Parker, et al. 1967]. Fluorescence spectra of (A) Kuwait Crude Oil in sea water; (B) Extract from phytoplankton presumably contaminated with Kuwait Crude Oil.

extent of instrument sophistication. Increased sensitivities are possible with newly developed instruments.

The instrumental precision and extraction precision had average standard deviations of $\pm$ 1.54 and $\pm$ 2.18 intensity units respectively (Table 3 and 4). These may even be improved upon once standard methods are established and streamlined for the fluorescence analysis of fuel oil on a routine basis. In order to ensure accuracy,standardization and calibration procedures are necessary on each run. Ideally, fluorescent standards for each fuel or wavelength of interest should be selected and the instrument should be calibrated for this wavelength region which is a function of the suspected fuel type in an unknown sample.

In this study, it was assumed that evaporation loss of low boiling compounds or fractions from fuel oils, produced no detectable change in fluorescence characteristics or intensity in agreement with a study by Thruston and Knight (1971). Parker (1970) also supports this idea since according to his paper, the fluorescent components are almost completely nonvolatile and, therefore, total fluorescence is constant regardless of evaporation, assuming no concentration effect. On the other hand, this hypothesis perhaps should be tested in future research.

Thruston and Knight (1970) and Parker (1970) also considered the effects of solar decomposition, leaching, oxidation and microbial action on fuel oil spills. There appears to be degradation in fluorescence characteristics

TABLE 5

Fluorescence Excitation and Emission Data
for Petroleum and Petroleum Products

Investigator	Sample	Excitation	Fluorescence
Shtegman (1966)	Petroleum products.	365 nm	450-500 nm
Parker and Barnes (1960)	Compressor lubricant.	248 nm	333-384 nm
		286 nm	333-384 nm
	Crude oil.	250 nm	350-400 nm
	Auto engine lubricant.	250 nm	360 nm
	Auto Diesel fuel.	250 nm	300-350 nm
	Auto Petrol.	250 nm	300-320 nm
Hornig (1971)	Fuel Oil #2	322 nm	351 nm
Parker, et al. (1967)	Kuwait Crude	250 nm	360 nm
Smith (1968	Crude Oil	400 nm	450 nm
Riecker (1962)	Crude Oil	unknown	440-630 nm
Thruston and Knight (1970)	Crude and semi refined fuel oil.	340 nm	386 nm
Howard (1972)	NSFO	320 nm	350, 410 nm
		340 nm	410 nm
		400 nm	450 nm
	JP-4	250 nm	290, 325 nm
		270 nm	290, 325 nm
		280 nm	340 nm
	JP-5	250 nm	290 nm
		270 nm	290 nm
		280 nm	290, 340 nm
	Diesel	250 nm	340 nm
		270 nm	340 nm
		280 nm	340 nm
	Distillate	290 nm	330nm,315nm, 340 nm
		240 nm	330 nm

and intensity with time of exposure, so for this reason, it would be advisable to sample a new oil spill quickly to support positive identification of the pollutant and pollutor. It is possible that water sampled at some depth may escape these effects should it reach a protective depth before any significant degradation occurs.

Further support for the application of natural fluorescence identification of fuels is the work done by Thruston and Knight (1971). Different samples of the same general fuel type were identified on the basis of two parameters for each fuel; the ratio of shoulder to peak fluorescence intensity for each undiluted fuel and the shoulder to peak ratio for various dilutions of the same fuel (Fig. 38 and 39). Variations within the same fuel were detected. Samples from an actual oil spill were examined with this method and four other standard identification methods. All were in agreement and the fuel was unambiguously identified. The application of this technique to the problem of detection of fuels as diverse as the naval fuels examined in this study should be a source of additional corroborating data.

The ability to identify the source and type of oil in an oil spill on a beach, in a river, a harbor or in the open ocean is fundamental to the effective enforcement of water pollution control procedures and statutes already in effect. There will be occasions when the only requirement is to monitor a process, such as bilge water discharge or ship ballast discharges or for early warning of fuel oil contam-

ination in a regional environment. At times, only the presence of fuel and its possible source will be required.

The results of this study can be applied to all of these situations. The characteristic excitation and fluorescence wavelengths determined for the five naval fuels will allow proper selection of filters for operation of low cost, simple filter fluorometers such as the Turner 111.

Quantitative information is required for base data studies on fuel contamination levels for environmental quality control or for cryptic long term effects on biological processes which may be toxic or produce subtle unwanted alteration of natural phenomena. Quantities as low as 0.1 ng/ml (0.1 ppb) may be detected and the potential exists for sensitivities as high as parts per trillion.

The extraction techniques developed in this study may yield a workable method for the determination of absolute concentration levels. More work in this area will be required to establish standard curves from which a concentration value can be obtained.

Work by Drushel and Sommers (1966) indicated that phosphorimetry can significantly enhance photoluminiscent identification of various compounds in petroleum. This author agrees in principle; however, fluorescence is a direct. inexpensive technique which can in itself be applied to at sea fuel analysis problems.

The results of this study show that passive detection and identification of naval fuels is possible by fluorescence

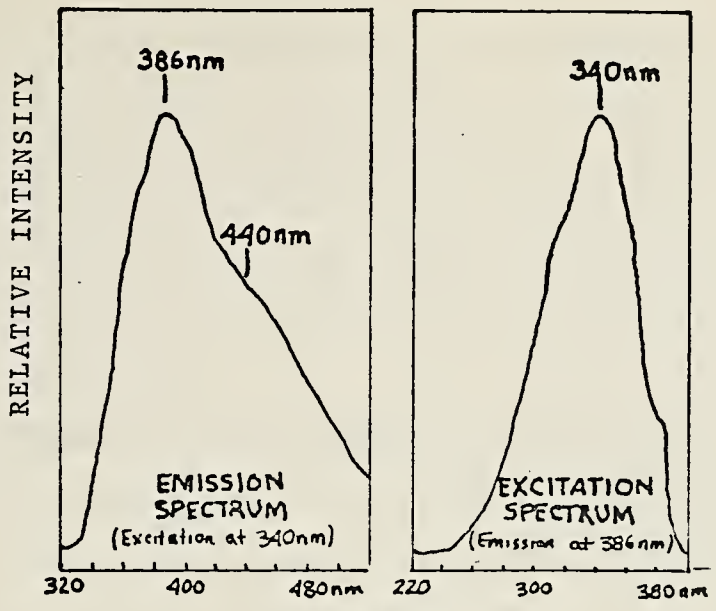

Fig. 38. Fluorescence and excitation spectra of a class of fuel oils which have a peak emission at 386 nm and a shoulder at 440 nm when excited at 340 nm [from Thruston and Knight 1970].

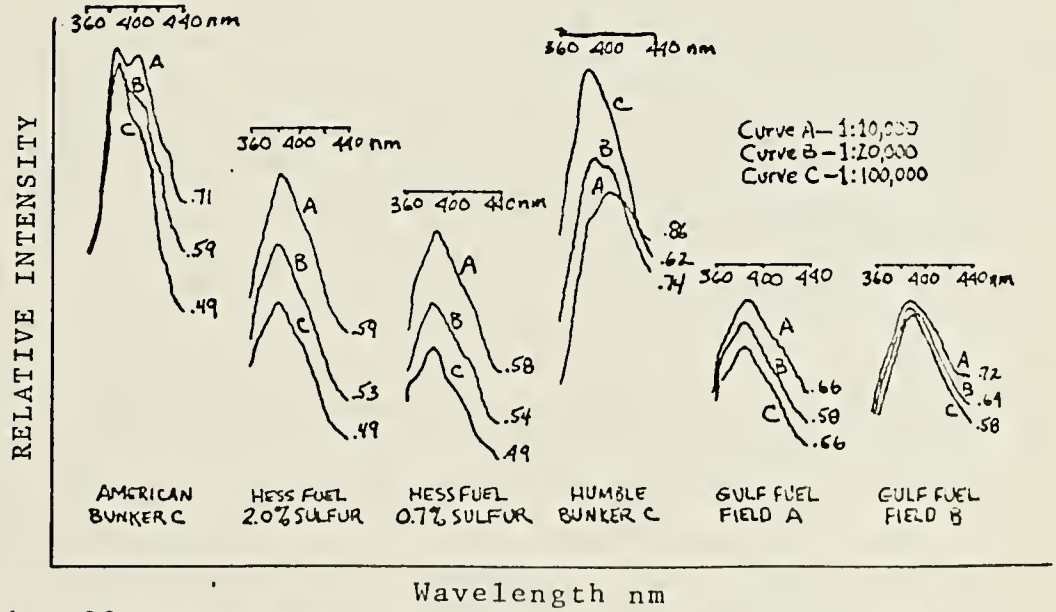

Fig. 39. Fluorescence spectra of various fuel oil showing peak intensities and shoulder to peak ratios for each fuel and dilutions of each fuel [from Thruston and Knight 1970].

spectrometry. The application of this method calls for some practical considerations. If bilge water or ballast water is to be monitored for contamination levels, it is quite within the possibilities of passive fluorescence techniques, without interfering processes such as contamination or environmental weathering.

The problem of oil spill analysis becomes more difficult with the later added effects. Efforts are now underway to legally trace fuel contamination to the vessel responsible. The method for accomplishing this must be cheap and unambiguous. Since at least four mutually supporting pieces of evidence are the minimum requirements for successful prosecution and conviction of offenders, the application of passive fluorescence tracing may not be enough alone.

For example, it is not known how much environmental weathering makes an oil spill unidentifiable. This means that supporting evidence must accompany excitation and fluorescence spectra of the oil spill. A promising alternate or supplement may well be "active tagging" or the addition of some known and readily identifiable fluorophor to the oil. This may be thought of as an identification "license plate."

"The added material must satisfy several criteria: it must be soluble or dispersible in oil and insoluble and nondispersible in water; it must be easily detectible in extreme dilution; it must be chemically and physically stable in both spilled and unspilled oil; it must not interfere

with the commercial uses of petroleum; and it must not be too expensive." [Horowitz, et al. 1971].

In "passive tagging," the oil slick must provide all of the information for its own identification by fluorescence; in other words, it must show its "fingerprint."

The addition of well-characterized fluorophors to fuel oil is possible today. Small measured quantities can be added to the oil as it is loaded on a ship with a metering device. One or more distinct fluorescent "license plates" could be added for positive identification of the fuel oil and the carrier by fluorescence analysis. By this method, the required, separate, supporting pieces of evidence could be quickly and reliably collected for use in any oil spill situation.

VI. CONCLUSIONS

The value of this technique for fuel oil contamination control and detection presents some interesting possibilities. Fluorescence techniques for active ("license plates") or passive ("fingerprints") could be used either separately or in support of one another in such areas as the quality control of overboard discharge of ballasting water from naval ships. An early warning system of high oil concentration in this water could actuate a quick acting automatic control valve to prevent discharge of potentially dangerous fuel oil contamination. This could be accomplished with realtively inexpensive filter instruments set at characteristic wavelengths for the fuel oil it would monitor. "Passive fluorescence" techniques would be sufficient for this application.

For oil spill detection, simple passive techniques are all that would be required; however, for the positive identification of the pollutant and pollutor, a combination of "active" and "passive tagging" would be appropriate. "Passive tagging" would be utilized to establish background fluorescence for all regions of interest. "Active and passive tagging" would be utilized for the gathering of sufficient identification information to make a strong legal case for the positive identification of the responsible parties.

The Navy would profit from establishing base data for the present levels of fuel oil contamination from which to measure the effectiveness of newly instituted preventive methods and cleanup programs.

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ABSTRACT

Fluorescence and Excitation spectra of Navy Standard Fuel Oil (NSFO), Navy Distillate Fuel (ND), Diesel Fuel and Navy Aircraft fuels (JP-4 and JP-5) were obtained with the Turner 210 Absolute Spectrofluorometer. Excitation spectra (peaks at 320 nm, 240 nm, 250 nm, 270 nm, 250 nm respectively) and Fluorescence spectra (peaks at 350, 410 nm, 330 nm, 340 nm, 240, 325 nm 240 nm respectively) are characteristic and may allow selective identification of these fuels. Quantitative determinations by fluorescence analysis of ND fuel oil extracted from sea water samples, with cyclohexane, showed saturation values of approximately 11 ppm. An all glass, in-situ vacuum filtering water sampler was designed and built for collection of filtered (.45μ glass) noncontaminated sea water samples for the Fluorescence analysis determination of the natural background fluorescence of the Monterey Bay region. Fluorescence spectra of sea water from Monterey Bay, obtained on board R/V ACANIA, and samples from the Arctic Ocean, showed broad banded emission in the region of 450 nm.

14. KEY WORDS	LINK A		LINK B		LINK C	
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naval fuels						
marine oil pollution						
dissolved organics						
fluorescence spectrometry						
sea water sampler						
marine fluorophors						

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